

## PATENT ABSTRACTS OF JAPAN

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## (54) POSITIVE RESIST COMPOSITION

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive resist composition having satisfactory transmittance when a source of light with 157 nm is used, having a wide defocus latitude, less liable to cause line edge roughness, free of concern for negative formation because a resist film is substantially thoroughly dissolved when developed with a developer and ensuring slight trailing of a line-and-space pattern.

SOLUTION: The positive resist composition comprises (A) a fluorine group- containing resin, which has a structure substituted with a fluorine atom in the main chain and/or side chain of polymer skeleton and a group that is decomposed by the action of an acid to increase solubility in an alkali developer and (B) an acid generator which generates an acid upon irradiation of an actinic ray or radiation, and the acid generator (B) is a sulfonium salt containing no aromatic ring or a compound having a phenacylsulfonium salt structure.

## LEGAL STATUS

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examiner's decision of rejection or application converted  
registration]

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**CLAIMS**

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[Claim(s)]

[Claim 1] (A) The positive-resist constituent characterize by to be the compound which have the sulfonium salt or the phenacyl sulfonium-salt structure where of have the structure which the fluorine atom permuted by the principal chain and/or the side chain of a polymer frame, and an operation of an acid decompose, and contain the acid generator which generate an acid by the exposure of the fluorine radical content resin which have the radical which increase the solubility to an alkali developer and (B) activity beam of light, or a radiation, and the (B) acid generator do not have a ring.

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive-resist constituent used suitable for micro lithography processes, such as manufacture of a VLSI and a high capacity microchip, and other photofabrication processes. Furthermore, it is related with the positive-resist constituent which can form in detail the pattern made highly minute using vacuum-ultraviolet light 160nm or less.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a quarter micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. As one of the means which attains detailed-ization of a pattern, short wavelength-ization of the exposure light source used in the case of the pattern formation of a resist is known.

[0003] For example, i line (365nm) of a high pressure mercury vapor lamp has been used for manufacture of the semiconductor device of the degree of integration to 64M bit as the light source to current. As a positive resist corresponding to this light source, many constituents containing the naphthoquinonediazide compound as novolak resin and a sensitization object were developed, and sufficient result has been stored in processing of the line breadth to about 0.3 micrometers. Moreover, instead of i line, KrF excimer laser light (248nm) has been adopted as manufacture of the semiconductor device of a 256 M bit or more degree of integration as the exposure light source. Furthermore, in order to form use of the ArF excimer laser light (193nm) which is the light source of short wavelength, and a pattern 0.1 more micrometers or less from recent years for the purpose of semi-conductor manufacture of the degree of integration beyond 1G bit, use of F2 excimer-laser light (157nm) is considered.

[0004] According to short-wavelength-izing of these light sources, the constituent and its compound structure of a resist ingredient are also changing a lot. That is, in the resist containing conventional novolak resin and a conventional naphthoquinonediazide compound, since the absorption in a 248nm far-ultraviolet field was large, light stopped fully easily being able to reach to a resist pars basilaris ossis occipitalis, and only the pattern of a taper configuration was obtained by low sensibility. In order to solve such a problem, the constituent which combined the compound (photo-oxide generating agent) which generates an acid in the exposure of far-ultraviolet light, and the so-called chemistry magnification mold resist came to be developed, using the resin which made the basic frame small Pori (hydroxystyrene) of absorption in 248nm field, and was protected by the acidolysis radical as a principal component.

By the catalyst decomposition reaction of the acid generated in the exposure section, since a chemistry magnification mold resist changes the solubility over a developer, it can form a high resolution pattern by high sensitivity.

[0005] However, since the compound which has an aromatic series radical essentially had big absorption to 193nm wavelength field when ArF excimer laser light (193nm) is used, engine performance sufficient by the above-mentioned chemistry magnification mold resist was not obtained.

[0006] It replaces with the acidolysis nature resin which introduced into the principal chain or side chain of a polymer the alicyclic structure which does not have absorption for the acidolysis nature resin which makes Pori (hydroxystyrene) a basic frame in 193nm to this problem, and amelioration of a chemistry magnification mold resist is achieved.

[0007] However, to F2 excimer-laser light (157nm), it became clear also in the above-mentioned alicycle mold resin that absorption of 157nm field is large and inadequate for obtaining the pattern 0.1 micrometers or less made into the purpose. On the other hand, it is reported by nonpatent literature 1 (Proc.SPIE.Vol.3678.13 page (1999)) that the resin which introduced the fluorine atom (perfluoro structure) has sufficient transparency for 157nm. The structure of an effective fluoro resin Nonpatent literature 2 (Proc.SPIE.Vol.3999.330 page (2000)), It is come to propose nonpatent literature 3 (pages 357 of said (2000)), nonpatent literature 4 (pages 365 of said (2000)), the patent reference 1 (WO -00/No. 17712), etc. However, amelioration of spreading nature (homogeneity of a spreading side) and control of a development defect were also desired for unique water-repellent \*\* oil-repellent property which cannot say that the dry etching-proof nature of the resist which has these fluoro resins is not necessarily enough, and originates in perfluoro structure. The positive-resist constituent which contains a sulfonium salt system compound as an acid generator is indicated by the patent reference 2 (the Europe patent application public presentation 1041442ANo. 1 specification), the patent reference 3 (the Europe patent application public presentation 1113334ANo. 1 specification), and the patent reference 4 (the Europe patent application public presentation 1207423ANo. 1 specification). However, as for the conventional resist constituent, amelioration was desired about skirt length of defocusing latitude, negative-izing, the Rhine edge roughness, Rhine, and a tooth-space pattern.

[0008] That is, if the processing dimension of a pattern makes it detailed and the resolving power of lithography comes to carry out a limitation, since it will become difficult to secure sufficient defocusing latitude, a resist with large defocusing latitude has come to be desired further. Here, the resist with large defocusing latitude means what has small fluctuation of the Rhine width of face accompanying a focal gap.

[0009] Moreover, if the processing dimension of a pattern makes it detailed and the contrast of image formation runs short, since the border area of an unexposed part and the exposure section will become ambiguous and homogeneous (the Rhine edge roughness) aggravation of the edge of the Rhine pattern will become remarkable, this solution came to be desired.

[0010]

[Nonpatent literature 1] Pros S PIAII (Proc.SPIE.) -- Vol.3678.13 page (1999)

[Nonpatent literature 2] Pros S PIAII (Proc.SPIE.) -- Vol.3999.330 page (2000)

[Nonpatent literature 3] Pros S PIAII (Proc.SPIE.) -- Vol.3999.357 page (2000)

[Nonpatent literature 4] Pros S PIAII (Proc.SPIE.) -- Vol.3999.365 page (2000)

[Patent reference 1] International public presentation/[ 00th ] No. 17712 pamphlet (WO -00/No. 17712)

[Patent reference 2] The Europe patent application public presentation 1041442ANo. 1 specification [the patent reference 3] The Europe patent application public presentation 1113334ANo. 1 specification [the patent reference 4] The Europe patent application public presentation 1207423ANo. 1 specification [0011]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering 160nm or less and the especially suitable positive-resist constituent for use of the exposure light source of F2 excimer-laser light (157nm), and specifically shows permeability sufficient at the time of 157nm light source use, and its defocusing latitude is large, and it is to offer the positive-resist constituent which the resist film dissolves completely substantially when negatives are developed with a developer, and does not have concern of negative-izing. Moreover, permeability sufficient at the time of 157nm light source use is shown, and defocusing latitude is large, and it is hard to generate the Rhine edge roughness, and is in offering a positive-resist constituent with small skirt length of Rhine and a tooth-space pattern. [0012]

[Means for Solving the Problem] this invention person etc. reached [ being splendidly attained because the purpose of this invention uses the following specific constituents, and ] a header and this invention, as a result of inquiring wholeheartedly with careful attention to many above-mentioned properties. That is, this invention is the following configuration.

[0013] (1) The positive-resist constituent characterize by to be the compound which have the sulfonium salt or the phenacyl sulfonium-salt structure where of have the structure which the fluorine atom permuted by the principal chain and/or the side chain of (A) polymer frame, and an operation of an acid decompose, and contain the acid generator which generate an acid by the exposure of the fluorine radical content resin which have the radical which increase the solubility to an alkali developer and (B) activity beam of light, or a radiation, and an acid generator (B) do not have a ring.

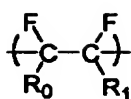
[0014] A desirable mode is indicated below.

(2) The resin of (A) the part chosen from a perfluoro alkylene group and a perfluoro arylene radical Whether it has in at least one principal chain of a polymer frame A perfluoroalkyl radical, The part chosen from the radical which protected the OH radical of a perfluoro aryl group, a hexafluoro-2-propanol radical, and a hexafluoro-2-propanol radical A positive-resist constituent given in the above (1) characterized by being fluorine radical content resin which it has in at least one side chain of a polymer frame.

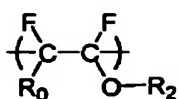
[0015] (3) The above (1) whose resin of (A) is characterized by having at least one repeat unit shown by general formula (I) - (X), or a positive-resist constituent given in (2).

[0016]

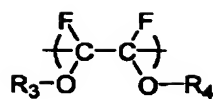
[Formula 1]



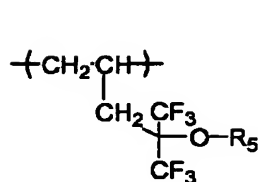
(I)



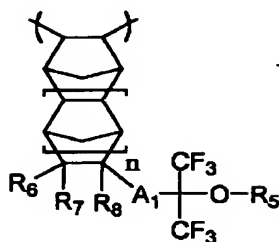
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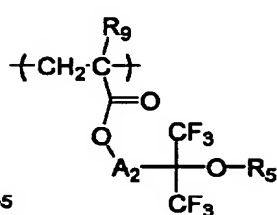
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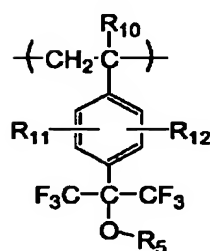
(IV)



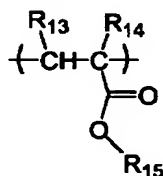
(V)



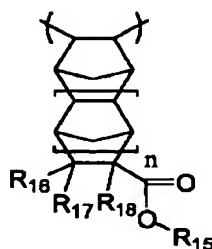
(VI)



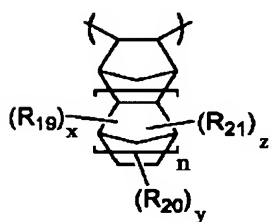
(VII)



(VIII)



(IX)



(X)

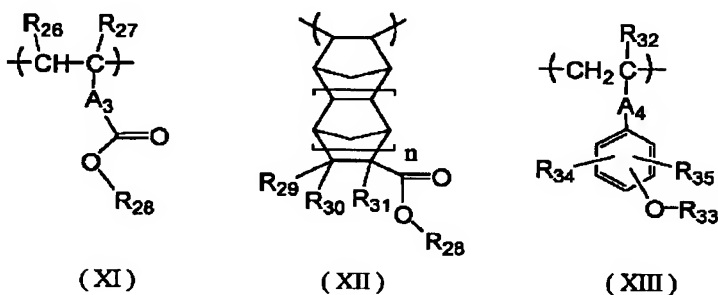
[0017] R0 and R1 express among a formula the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the fluorine atom, and the substituent, a cycloalkyl radical, or an aryl group. In addition, the perfluoroalkyl radical which has a substituent means the radical by which at least one fluorine atom of a perfluoroalkyl radical was permuted by other atoms or radicals. the following -- the same . R2-R4 express the alkyl group and perfluoroalkyl radical which may have the substituent, a cycloalkyl radical, or an aryl group. Moreover, R2, R3, and R4 may combine with R0, and R1 and R0, and a ring may be formed. R5 expresses the cycloalkyl radical of the alkyl group and perfluoroalkyl radical which may have the hydrogen atom and the substituent, a monocycle, or many rings, an acyl group, and an alkoxy carbonyl group. even if R6, R7, and R8 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, and the substituent, and an alkoxy group. R9 and R10 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. even if R11 and R12 are the same, they may differ from each other, and they express the alkyl group which may have a hydrogen atom, hydroxyl, a halogen atom, the

cyano group, the alkoxy group, the acyl group, or the substituent, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, or an aryl group. R13 and R14 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R15 expresses the cycloalkyl radical of the alkyl group and monocycle which have a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, or an aryl group. even if R16, R17, and R18 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent, an alkoxy group, and  $-\text{CO}-\text{O}-\text{R15}$ . even if R19, R20, and R21 are the same, they may differ from each other, and they express the cycloalkyl radical of the alkyl group and monocycle which have a hydrogen atom, a fluorine atom, and a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, an aryl group, or an alkoxy group. However, at least one of R19, R20, and the R21 is radicals other than a hydrogen atom. A1 and A2 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-\text{O}-\text{CO}-\text{R22}-$ ,  $-\text{CO}-\text{O}-\text{R23}-$ , and  $-\text{CO}-\text{N}(\text{R24})-\text{R25}-$ . even if R22, R23, and R25 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical. R24 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. n expresses 0 or 1 and x, and y and z express the integer of 0-4.

[0018] (4) A positive-resist constituent given in either of aforementioned (1) - (3) to which the resin of (A) is characterized by having at least one repeat unit further shown by general formula (XI) - (XIII).

[0019]

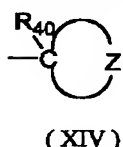
[Formula 2]



[0020] R26, R27, and R32 express among a formula the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R28 and R33 express the radical of  $-\text{C}(\text{R36})(\text{R37})(\text{R38})$ ,  $-\text{C}(\text{R36})(\text{R37})(\text{OR39})$ , or a formula (XIV).

[0021]

[Formula 3]



[0022] even if R29, R30, and R31 are the same, they may differ from each other, and they

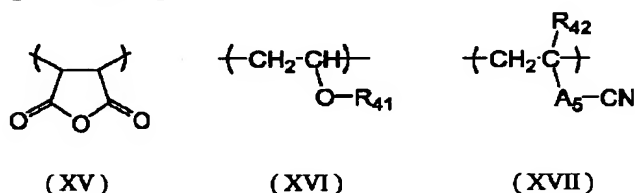


express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent, an alkoxy group, and  $-\text{CO}-\text{O}-\text{R}28$ . even if  $\text{R}34$  and  $\text{R}35$  are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, hydroxyl, a halogen atom, the cyano group, the alkoxy group, the acyl group, or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. even if  $\text{R}36$ ,  $\text{R}37$ ,  $\text{R}38$ , and  $\text{R}39$  are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an alkynyl group, an aralkyl radical, or an aryl group. 2 of  $\text{R}36$ ,  $\text{R}37$ , and  $\text{R}38$  or 2 of  $\text{R}36$ ,  $\text{R}37$ , and  $\text{R}39$  may join together, and a ring may be formed. Moreover, the oxo-radical may be contained to the formed ring.  $\text{R}40$  expresses the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an alkynyl group, an aralkyl radical, or an aryl group.  $\text{A}3$  and  $\text{A}4$  express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-\text{O}-\text{CO}-\text{R}22-$ ,  $-\text{CO}-\text{O}-\text{R}23-$ , and  $-\text{CO}-\text{N}(\text{R}24)-\text{R}25-$ . even if  $\text{R}22$ ,  $\text{R}23$ , and  $\text{R}25$  are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical.  $\text{R}24$  expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group.  $\text{Z}$  expresses the atomic group which constitutes the alicyclic radical of a monocycle or many rings to a carbon atom and  $**$ .  $n$  expresses 0 or 1.

[0023] (5) A positive-resist constituent given in either of aforementioned (1) – (4) to which the resin of (A) is characterized by having at least one repeat unit further shown by general formula (XV) – (XVII).

[0024]

[Formula 4]

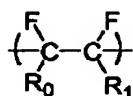


[0025]  $\text{R}41$  expresses among a formula the alkyl group and cycloalkyl radical which may have the substituent, an aralkyl radical, or an aryl group.  $\text{R}42$  expresses the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent.  $\text{A}5$  expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-\text{O}-\text{CO}-\text{R}22-$ ,  $-\text{CO}-\text{O}-\text{R}23-$ , and  $-\text{CO}-\text{N}(\text{R}24)-\text{R}25-$ .  $\text{R}22$ – $\text{R}25$  are synonymous with the above.

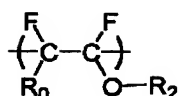
[0026] (6) A positive-resist constituent given in either of aforementioned (1) – (5) to which the resin of (A) is characterized by having at least one for the repeat unit indicated to be at least one by general formula (IV)– (VI) in the repeat unit shown by the following general formula (I) – (III).

[0027]

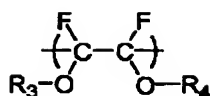
[Formula 5]



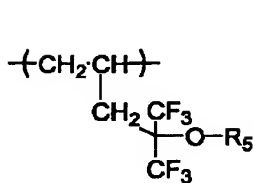
(I)



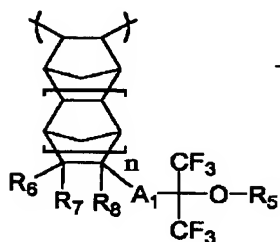
(II)



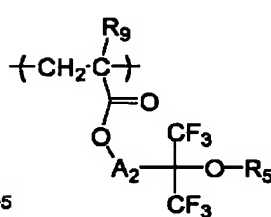
(III)



(IV)



(V)



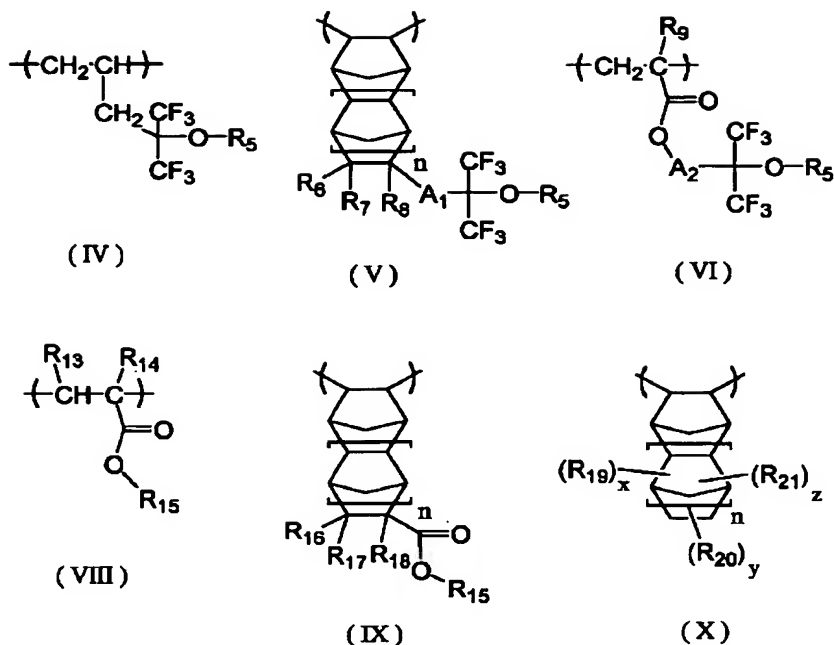
(VI)

[0028] R0 and R1 express among a formula the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the fluorine atom, and the substituent, a cycloalkyl radical, or an aryl group. R2–R4 express the alkyl group and perfluoroalkyl radical which may have the substituent, a cycloalkyl radical, or an aryl group. Moreover, R2, R3, and R4 may combine with R0, and R1 and R0, and a ring may be formed. R5 expresses the cycloalkyl radical of the alkyl group and perfluoroalkyl radical which may have the hydrogen atom and the substituent, a monocycle, or many rings, an acyl group, and an alkoxy carbonyl group. even if R6, R7, and R8 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, and the substituent, and an alkoxy group. R9 expresses the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. A1 and A2 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or –O–CO–R22–, –CO–O–R23–, and –CO–N(R24)–R25–. even if R22, R23, and R25 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical. R24 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. n expresses 0 or 1.

[0029] (7) A positive-resist constituent given in either of aforementioned (1) – (5) to which the resin of (A) is characterized by having at least one for the repeat unit indicated to be at least one by general formula (VIII)– (X) in the repeat unit shown by following general formula (IV)– (VI).

[0030]

[Formula 6]

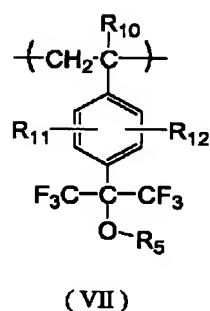
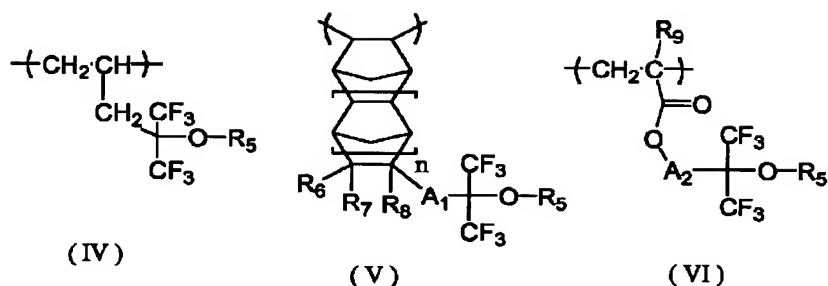


[0031] R5 expresses the cycloalkyl radical of the alkyl group and perfluoroalkyl radical which may have the hydrogen atom and the substituent, a monocycle, or many rings, an acyl group, and an alkoxy carbonyl group. even if R6, R7, and R8 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, and the substituent, and an alkoxy group. R9 expresses the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R13 and R14 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R15 expresses the cycloalkyl radical of the alkyl group and monocycle which have a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, or an aryl group. even if R16, R17, and R18 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent, an alkoxy group, and  $\text{-CO-O-R}_{15}$ . even if R19, R20, and R21 are the same, they may differ from each other, and they express the cycloalkyl radical of the alkyl group and monocycle which have a hydrogen atom, a fluorine atom, and a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, an aryl group, or an alkoxy group. However, at least one of R19, R20, and the R21 is radicals other than a hydrogen atom. A1 and A2 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $\text{-O-CO-R}_{22}\text{-}$ ,  $\text{-CO-O-R}_{23}\text{-}$ , and  $\text{-CO-N(R}_{24}\text{)-R}_{25}\text{-}$ . even if R22, R23, and R25 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical. R24 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. n expresses 0 or 1 and x, and y and z express the integer of 0-4.

[0032] (8) A positive-resist constituent given in either of aforementioned (1) - (5) to which the resin of (A) is characterized by having at least one for the repeat unit indicated to be at least one by general formula (XV) - (XVII) in the repeat unit shown by following general formula (IV) - (VII).

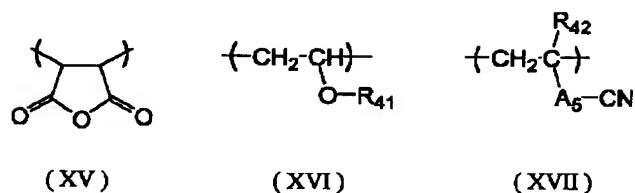
[0033]

[Formula 7]



[0034]

[Formula 8]



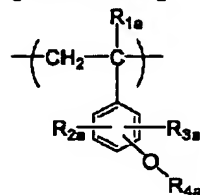
[0035] R5 expresses the cycloalkyl radical of the alkyl group and perfluoroalkyl radical which may have the hydrogen atom and the substituent, a monocycle, or many rings, an acyl group, and an alkoxy carbonyl group. even if R6, R7, and R8 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, and the substituent, and an alkoxy group. R9 and R10 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. even if R11 and R12 are the same, they may differ from each other, and they express the alkyl group which may have a hydrogen atom, hydroxyl, a halogen atom, the cyano group, the alkoxy group, the acyl group, or the substituent, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, or an aryl group. A1 and A2 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or -O-CO-R22-, -CO-O-R23-, and -CO-N(R24)-R25-. even if R22, R23, and R25 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical. R24 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. n expresses 0 or 1. R41 expresses the alkyl group and cycloalkyl radical which may have the

substituent, an aralkyl radical, or an aryl group. R42 expresses the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. A5 expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-O-CO-R22-$ ,  $-CO-O-R23-$ , and  $-CO-N(R24)-R25-$ .

[0036] (9) A positive-resist constituent given in (1) characterized by the resin of (A) being resin which has respectively the following general formula (IA) and (IIA) at least one repeat unit shown.

[0037]

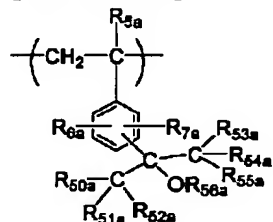
[Formula 9]



(IA)

[0038]

[Formula 10]

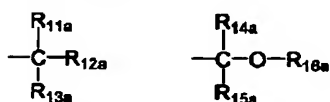


(IIA)

[0039] into a general formula (IA) (IIA), even if R1a and R5a are the same, they may differ from each other, and they express the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. even if R2a, R3a, R6a, and R7a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, a halogen atom, a cyano group, hydroxyl, or a substituent, an alkoxy group, an acyl group, an acyloxy radical, an alkenyl radical, an aryl group, or an aralkyl radical. even if R50 a-R55a is the same, it may differ, and it expresses the alkyl group which may have the hydrogen atom, the fluorine atom, or the substituent. However, at least one of R50 a-R55a expresses the alkyl group by which a fluorine atom or at least one hydrogen atom was permuted by the fluorine atom. R56a expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an acyl group, or an alkoxy carbonyl group. R4a expresses the radical of the following general formula (IVA) or (VA).

[0040]

[Formula 11]



(IVA)

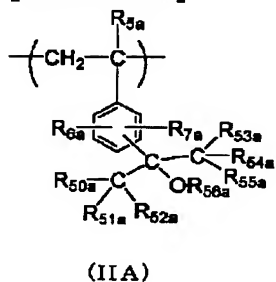
(VA)

[0041] among a general formula (IVA), even if R11a, R12a, and R13a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. among a general formula (VA), even if R14a and R15a are the same, they may differ from each other, and they express the alkyl group which may have the hydrogen atom or the substituent. R16a expresses the alkyl group and cycloalkyl radical which may have the substituent, an aralkyl radical, or an aryl group. Two of R14 a–R16a may join together, and a ring may be formed.

[0042] (10) A positive-resist constituent given in (1) characterized by the resin of (A) being resin which has respectively the following general formula (IIA) and (VIA) at least one repeat unit shown.

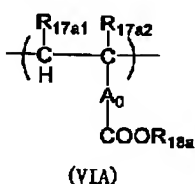
[0043]

[Formula 12]



[0044]

[Formula 13]

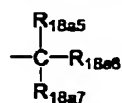


[0045] R5a expresses the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent among a general formula (IIA). even if R6a and R7a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, a halogen atom, a cyano group, hydroxyl, or a substituent, an alkoxy group, an acyl group, an acyloxy radical, an alkenyl radical, an aryl group, or an aralkyl radical. even if R50 a–R55a is the same, it may differ, and it expresses the alkyl group which may have the hydrogen atom, the fluorine atom, or the substituent. However, at least one of R50 a–R55a expresses the alkyl group by which a fluorine atom or at least one hydrogen atom was permuted by the fluorine atom. R56a expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an acyl group, or an alkoxy carbonyl group. Among a general formula (VIA), but you may differ and R17a1 and R17a2 express the same alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. R18a expresses –C (R18a1) (R18a2) (R18a3) or –C (R18a1) (R18a2) (OR 18a4). even if R18a1–R18a4 are the same, they may differ, and they express the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. Two of two or R18a1 of R18a1, R18a2, and R18a3, R18a2, and R18a4 may join together, and a ring may be formed. A0 expresses the divalent connection radical which may have single bond or a substituent.

[0046] (11) A positive-resist constituent given in (10) to which R18a is characterized by what is expressed with the following general formula (VIA-A) among the above-mentioned general formula (VIA).

[0047]

[Formula 14]



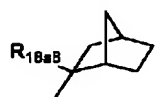
(VIA-A)

[0048] Among a general formula (VIA-A), but you may differ and R18a5 and R18a6 express the same alkyl group which may have the substituent. R18a7 express the cycloalkyl radical which may have the substituent.

[0049] (12) A positive-resist constituent given in (10) to which R18a is characterized by what is expressed with the following general formula (VIA-B) among the above-mentioned general formula (VIA).

[0050]

[Formula 15]



(VIA-B)

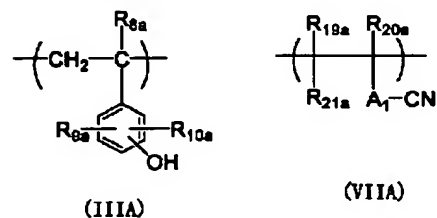
[0051] R18a8 express the alkyl group and alkenyl radical which may have the substituent, an alkynyl group, an aralkyl radical, or an aryl group among a general formula (VIA-B).

[0052] (13) (9) to which at least one of the R17a2 of R1a of a general formula (IA), R5a of a general formula (IIA), and a general formula (VIA) is characterized by being a trifluoromethyl radical, or a positive-resist constituent given in (10).

[0053] (14) A positive-resist constituent given in either of (9) - (13) to which the resin of (A) is characterized by having the following general formula (IIIA) or (VIIA) at least one repeat unit expressed further.

[0054]

[Formula 16]



[0055] R8a expresses the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent among a general formula (IIIA). even if R9a and R10a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent, an alkoxy group, an acyl group, an acyloxy radical, an alkenyl radical, an aryl group, or an aralkyl radical. among a general formula (VIIA), even if R19a and R20a are the same, they may differ

from each other, and they express the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. R21a expresses the alkyl group or -A1-CN radical which may have the hydrogen atom, the halogen atom, and the substituent. A1 expresses single bond or a divalent connection radical.

[0056] (15) A positive-resist constituent given in either of aforementioned (1) – (14) characterized by furthermore containing (C) Si system and/or a fluorochemical surfactant.

(16) A positive-resist constituent given in either of aforementioned (1) – (15) furthermore characterized by containing the compound which has a basic nitrogen atom as a (D) acid diffusion inhibitor.

[0057] (17) A positive-resist constituent given in either of aforementioned (1) – (16) characterized by being chosen from the compound of the sulfonium salt in which the compound of the (B) component generates a two or more carbon atomic numbers perfluoroalkyl sulfonic acid, a perfluoro aryl sulfonic acid, or the aryl sulfonic acid that the perfluoroalkyl radical permuted by the exposure of an activity beam of light or a radiation, or iodonium salt.

[0058] (18) A positive-resist constituent given in either of aforementioned (1) – (17) characterized by using vacuum-ultraviolet light 160nm or less as the exposure light source.

[0059]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

(A) fluorine radical content resin in [1] (A) fluorine radical content resin this invention It has the structure which the fluorine atom permuted in the principal chain and/or side chain of a polymer. And it is resin characterized by having the radical which decomposes according to an operation of an acid and increases the solubility to an alkali developer. The part preferably chosen from a perfluoro alkylene group and a perfluoro arylene radical Whether it has in at least one principal chain of a polymer frame A perfluoroalkyl radical, It is fluorine radical content resin which has the part chosen from the radical which protected the OH radical of a perfluoro aryl group, a hexafluoro-2-propanol radical, and a hexafluoro-2-propanol radical in at least one side chain of a polymer frame.

[0060] It is resin which specifically has at least one repeat unit shown by general formula (I) – (X), and is fluorine radical content resin which has the acidolysis nature machine which has at least one repeat unit preferably shown further by general formula (XI) – (XIII). Moreover, in order to control physical properties, such as permeability to the relative-degree-of-intimacy aquosity of fluorine radical content resin, a glass transition point, and exposure light, or in order to control the polymerization nature at the time of polymer composition, you may have at least one repeat unit originating in the vinyl compound containing the maleic anhydride, the vinyl ether, or the cyano group shown by general formula (XV) – (XVII).

[0061] R0 and R1 express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the fluorine atom, and the substituent, a cycloalkyl radical, or an aryl group among a general formula. R2–R4 express the alkyl group and perfluoroalkyl radical which may have the substituent, a cycloalkyl radical, or an aryl group. Moreover, R2, R3, and R4 may combine with R0, and R1 and R0, and a ring may be formed. R5 expresses the cycloalkyl radical of the alkyl group and perfluoroalkyl radical which may have the hydrogen atom and the substituent, a monocycle, or many rings, an acyl group, and an alkoxy carbonyl group. even if R6, R7, and R8 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, and the substituent, and an alkoxy group.

[0062] R9 and R10 express the same alkyl group or same halo alkyl group which may be [ but ]



different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. even if R11 and R12 are the same, they may differ from each other, and they express the alkyl group which may have a hydrogen atom, hydroxyl, a halogen atom, the cyano group, the alkoxy group, the acyl group, or the substituent, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, or an aryl group. R13 and R14 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent.

[0063] R15 expresses the cycloalkyl radical of the alkyl group and monocycle which have a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, or an aryl group. even if R16, R17, and R18 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent, an alkoxy group, and  $-\text{CO}-\text{O}-\text{R15}$ . even if R19, R20, and R21 are the same, they may differ from each other, and they express the cycloalkyl radical of the alkyl group and monocycle which have a hydrogen atom, a fluorine atom, and a fluorine atom, or many rings, an alkenyl radical, an aralkyl radical, an aryl group, or an alkoxy group. However, at least one of R19, R20, and the R21 is radicals other than a hydrogen atom.

[0064] A1 and A2 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-\text{O}-\text{CO}-\text{R22}-$ ,  $-\text{CO}-\text{O}-\text{R23}-$ , and  $-\text{CO}-\text{N}(\text{R24})-\text{R25}-$ . even if R22, R23, and R25 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have single bond or a ether group, an ester group, an amide group, a urethane group, or an ureido radical, a cyclo alkylene group, or an arylene radical. R24 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group.

[0065] R26, R27, and R32 express the same alkyl group or same halo alkyl group which may be [ but ] different and may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R28 and R33 express the radical of  $-\text{C}(\text{R36})(\text{R37})(\text{R38})$ ,  $-\text{C}(\text{R36})(\text{R37})(\text{OR39})$ , or the above-mentioned general formula (XIV). even if R29, R30, and R31 are the same, they may differ from each other, and they express the alkyl group and perfluoroalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent, an alkoxy group, and  $-\text{CO}-\text{O}-\text{R28}$ .

[0066] even if R34 and R35 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, hydroxyl, a halogen atom, the cyano group, the alkoxy group, the acyl group, or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. even if R36, R37, R38, and R39 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an alkynyl group, an aralkyl radical, or an aryl group. 2 of R36, R37, and R38 or 2 of R36, R37, and R39 may join together, and a ring may be formed. Moreover, the oxo-radical may be contained to the formed ring. R40 expresses the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an alkynyl group, an aralkyl radical, or an aryl group.

[0067] A3 - A4 express the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-\text{O}-\text{CO}-\text{R22}-$ ,  $-\text{CO}-\text{O}-\text{R23}-$ , and  $-\text{CO}-\text{N}(\text{R24})-\text{R25}-$ . Z expresses the atomic group which constitutes the alicyclic radical of a monocycle or many rings to a carbon atom and \*\*.

[0068] R41 expresses the alkyl group and cycloalkyl radical which may have the substituent, an

aralkyl radical, or an aryl group. R42 expresses the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. A5 expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or  $-O-CO-R22-$ ,  $-CO-O-R23-$ , and  $-CO-N(R24)-R25-$ . n expresses 0 or 1 and x, and y and z express the integer of 0-4.

[0069] Moreover, the resin which has respectively the above-mentioned general formula (IIA) and (VIA) at least one repeat unit shown can be mentioned to the resin list which has respectively the above-mentioned general formula (IA) and (IIA) at least one repeat unit shown as still more desirable fluorine radical content resin (A) in this invention. These fluorine radical content resin (A) may have the above-mentioned general formula (IIIA) or (VIIA) at least one repeat unit shown further. As for these fluorine radical content resin (A), it is desirable the above-mentioned general formula (VIA-A) or (VIA-B) that R18a in a general formula (VIA) is expressed. Moreover, as for these fluorine radical content resin (A), it is desirable that at least one of the R17a2 of R1a of a general formula (IA), R5a of a general formula (IIA), and a general formula (VIA) is a trifluoromethyl radical.

[0070] The fluorine radical content resin (A) which has respectively a general formula (IIA) and (VIA) at least one repeat unit shown in the fluorine radical content resin (A) list which has respectively a general formula (IA) and (IIA) at least one repeat unit shown may have the repeat unit further shown by said general formula (I) - (V).

[0071] into a general formula (IA) (IIA), even if R1a and R5a are the same, they may differ from each other, and they express the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. even if R2a, R3a, R6a, and R7a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, a halogen atom, a cyano group, hydroxyl, or a substituent, an alkoxy group, an acyl group, an acyloxy radical, an alkenyl radical, an aryl group, or an aralkyl radical. even if R50 a-R55a is the same, it may differ, and it expresses the alkyl group which may have the hydrogen atom, the fluorine atom, or the substituent. However, at least one of R50 a-R55a expresses the alkyl group by which a fluorine atom or at least one hydrogen atom was permuted by the fluorine atom. R56a expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an acyl group, or an alkoxy carbonyl group, and it is desirable that it is a hydrogen atom. R4a expresses the radical of the above-mentioned general formula (IVA) or (VA).

[0072] among a general formula (IVA), even if R11a, R12a, and R13a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. among a general formula (VA), even if R14a and R15a are the same, they may differ from each other, and they express the alkyl group which may have the hydrogen atom or the substituent. R16a expresses the alkyl group and cycloalkyl radical which may have the substituent, an aralkyl radical, or an aryl group. Two of R14 a-R16a may join together, and a ring may be formed.

[0073] Among a general formula (VIA), but you may differ and R17a1 and R17a2 express the same alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. R18a expresses  $-C(R18a1)(R18a2)(R18a3)$  or  $-C(R18a1)(R18a2)(OR18a4)$ . even if R18a1-R18a4 are the same, they may differ, and they express the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group. Two of two or R18a1 of R18a1, R18a2, and R18a3, R18a2, and R18a4 may join together, and a ring may be formed. A0 expresses the divalent connection

radical which may have single bond or a substituent, and it is desirable that it is single bond.

[0074] Among a general formula (VIA-A), but you may differ and R18a5 and R18a6 express the same alkyl group which may have the substituent. R18a7 express the cycloalkyl radical which may have the substituent.

[0075] R18a8 express the alkyl group and alkenyl radical which may have the substituent, an alkynyl group, an aralkyl radical, or an aryl group among a general formula (VIA-B).

[0076] R8a expresses the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent among a general formula (IIIA). even if R9a and R10a are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent, an alkoxy group, an acyl group, an acyloxy radical, an alkenyl radical, an aryl group, or an aralkyl radical. among a general formula (VIIA), even if R19a and R20a are the same, they may differ from each other, and they express the alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, or the substituent. R21a expresses the alkyl group or -A1-CN radical which may have the hydrogen atom, the halogen atom, and the substituent. A1 expresses single bond or a divalent connection radical.

[0077] As the above-mentioned alkyl group, it is the alkyl group of 1-8 carbon numbers, for example, and, specifically, a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, a hexyl group, a 2-ethylhexyl radical, and an octyl radical can be mentioned preferably. As a cycloalkyl radical, a monocycle mold may be used, and a polycyclic mold may be used. As a monocycle mold, it is the thing of 3-8 carbon numbers, for example, a PUCHIRU radical and a cyclo octyl radical can be preferably mentioned to a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, and cyclo. As a polycyclic mold, it is the thing of 6-20 carbon numbers, for example, an adamantyl radical, a norbornyl radical, an isoboronil radical, a camphor nil radical, a JISHIKURO pentyl radical, alpha-PINERU radical, a tricyclo deca nil radical, the TETOSHI clo dodecyl, a loss TANIRU radical, etc. can be mentioned preferably. However, the carbon atom in the cycloalkyl radical of the above-mentioned monocycle or many rings may be permuted by hetero atoms, such as an oxygen atom.

[0078] As a perfluoroalkyl radical, it is the thing of 4-12 carbon numbers, for example, and perfluoro butyl, a perfluoro hexyl group, a perfluoro octyl radical, a perfluoro octyl ethyl group, the perfluoro dodecyl, etc. can specifically be raised preferably. As a halo alkyl group, it is the halo alkyl group of 1-4 carbon numbers, for example, and a chloro methyl group, a chloro ethyl group, a chloropropyl radical, a chlorobutyl radical, a bromomethyl radical, a BUROMO ethyl group, etc. can specifically be mentioned preferably.

[0079] As an aryl group, it is the aryl group of 6-15 carbon numbers, for example, and, specifically, a phenyl group, a tolyl group, a dimethylphenyl radical, 2 and 4, 6-trimethyl phenyl radical, a naphthyl group, an anthryl radical, 9, 10-dimethoxy anthryl radical, etc. can be mentioned preferably. As an aralkyl radical, it is the aralkyl radical of 7-12 carbon numbers, for example, and, specifically, benzyl, a phenethyl radical, a naphthyl methyl group, etc. can be mentioned preferably. As an alkenyl radical, it is the alkenyl radical of 2-8 carbon numbers, for example, and, specifically, a vinyl group, an allyl group, a butenyl group, and a cyclohexenyl group can be mentioned preferably.

[0080] As an alkoxy group, it is the alkoxy group of 1-8 carbon numbers, for example, and, specifically, a methoxy group, an ethoxy radical, n-propoxy group, an iso-propoxy group, a butoxy radical, a pentoxy radical, an allyloxy radical, an octoxy radical, etc. can be mentioned preferably. As an acyl group, it is the acyl group of 1-10 carbon numbers, for example, and,

specifically, a formyl group, an acetyl group, a propanoyl radical, a butanoyl radical, a pivaloyl radical, an octanoyl group, benzoyl, etc. can be mentioned preferably. As an acyloxy radical, the acyloxy radical of 2–12 carbon numbers is desirable, for example, can mention an acetoxyl radical, a propionyloxy radical, a benzoyloxy radical, etc. As an alkynyl group, the alkynyl group of carbon numbers 2–5 is desirable, for example, can mention an ethynyl group, a propynyl radical, a butynyl radical, etc. As an alkoxy carbonyl group, the 2nd class of the alkoxy carbonyl group of the 3rd class is more preferably mentioned for an i-propoxy carbonyl group, a t-butoxycarbonyl group, t-friend ROKISHI carbonyl group, a 1-methyl-1-cyclohexyloxy carbonyl group, etc. As a halogen atom, a fluorine atom, a chlorine atom, a bromine atom, iodine atom, etc. can be mentioned, for example.

[0081] The thing of 1–8 carbon numbers, such as the methylene group which may have the substituent preferably as an alkylene group, ethylene, a propylene radical, a butylene radical, a hexylene radical, and an octylene radical, is mentioned. The thing of 2–6 carbon numbers, such as an ETENIREN radical which may have the substituent preferably as an alkenylene group, a pro PENIREN radical, and a butenylene radical, is mentioned. The thing of 5–8 carbon numbers, such as a cyclo pentene radical and a cyclo hexylene radical, which may have the substituent preferably as a cyclo alkylene group is mentioned. The thing of 6–15 carbon numbers, such as a phenylene group which may have the substituent preferably as an arylene radical, a tolylene radical, and a naphthylene radical, is mentioned.

[0082] A divalent connection radical expresses the divalent alkylene group and cyclo alkylene group which may have the substituent, an alkenylene group, an arylene radical or  $-O-CO-R22a-$ ,  $-CO-O-R23a-$ , or  $-CO-N(R24a)-R25a-$ . even if R22a, R23a, and R25a are the same, they may differ from each other, and they express the divalent alkylene group when you may have single bond or a ether group, the ester group, the amide group, the urethane group, or the ureido radical, an alkenylene group, a cyclo alkylene group, or an arylene radical. R24a expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom or the substituent, an aralkyl radical, or an aryl group.

[0083] As a ring which R2, R3, and R4 combined with R0, and R1 and R0, and was formed, it is five to 7 membered-ring, for example, and pentane ring [ which the fluorine specifically permuted ], hexane ring, furan ring, dioxo Norian ring, 1, and 3-dioxolane ring etc. is mentioned. As a ring combined and formed, 2 of R36–R38 or 2 of R36–R37, and R39 are three to 8 membered-ring, for example, and they can specifically mention preferably a cyclopropane ring, a cyclopentane ring, a cyclohexane ring, a furan ring, a pyran ring, etc.

[0084] As a ring which two of 2 of R14 a–R16a, 2 of R18a1–R18a3 or R18a1, R18a2, and R18a4 combine and form Three to 8 membered-ring is desirable. For example, a cyclopropane ring, a cyclopentane ring, Cyclohexane ring, tetramethylene oxide ring, pentamethylene oxide ring, hexamethylene oxide ring, furan ring, pyran ring, dioxo Norian ring, 1, and 3-dioxolane ring etc. can be mentioned.

[0085] Z expresses the atomic group which constitutes the alicyclic radical of a monocycle or many rings, as an alicyclic radical formed, is the thing of 3–8 carbon numbers as a monocycle mold, for example, can mention a PUCHIRU radical and a cyclo octyl radical preferably to a cyclo propyl group, a cyclopentylic group, a cyclohexyl radical, and cyclo. As a polycyclic mold, it is the thing of 6–20 carbon numbers, for example, an adamantyl radical, a norbornyl radical, an isoboronyl radical, a camphor nil radical, a JISHIKURO pentyl radical, a–PINERU radical, a tricyclo deca nil radical, the TETOSHI clo dodecyl, a loss TANIRU radical, etc. can be mentioned preferably.

[0086] moreover, as a substituent permuted by these radicals An alkyl group, a cycloalkyl radical, an aryl group, the amino group, an amide group, What [ has active hydrogen, such as an ureido radical, a urethane group, hydroxyl, and a carboxyl group ] a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom) and an alkoxy group (a methoxy group --) thioether radicals, such as an ethoxy radical, a propoxy group, and a butoxy radical, and an acyl group (an acetyl group --) Acyloxy radicals (an acetoxyl radical, a propanoyloxy radical, benzoyloxy radical, etc.), such as a propanoyl radical and benzoyl, alkoxy carbonyl groups (a methoxycarbonyl group, an ethoxycarbonyl radical, propoxy carbonyl group, etc.), a cyano group, a nitro group, etc. are mentioned. Here, although what showed the alkyl group, the cycloalkyl radical, and the aryl group above is mentioned, the alkyl group may be further permuted by the fluorine atom and the cycloalkyl radical.

[0087] As a radical which decomposes according to the operation of an acid included in the fluorine radical content resin of this invention, and increases the solubility to an alkali developer For example,  $-O-C(R36)(R37)(R38)$ ,  $-O-C(R36)(R37)(OR39)$ ,  $-O-COO-C(R36)(R37)(R38)$ ,  $-O-C(R01)(R02)COO-C(R36)(R37)(R38)$ ,  $-COO-C(R36)(R37)(R38)$ ,  $-COO-C(R36)(R37)(OR39)$ , etc. are mentioned. R36-R39 are synonymous with the above, and R01 and R02 express the alkyl group which may have the hydrogen atom and the substituent shown by the above, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, or an aryl group.

[0088] As a desirable example of the above-mentioned acidolysis nature machine, t-butyl, t-amyl group, A 1-alkyl-1-cyclohexyl radical, a 2-alkyl-2-adamantyl radical, The ether group or ester groups of the 3rd class alkyl group, such as a 2-adamantyl-2-propyl group and a 2-(4-methylcyclohexyl)-2-propyl group, Acetal radicals, such as a 1-alkoxy-1-ethoxy radical and a tetrahydropyranyl group, or an acetal ester group, t-alkyl carbonate radical, t-alkyl carbonyl methoxy group, etc. are mentioned preferably.

[0089] the sum total of the content of the repeat unit shown by general formula (I) - (X) -- under [ all ] a polymer presentation -- setting -- general -- 10 - 80-mol % -- desirable -- 30 - 70-mol % -- it is used in [ 35 - 65 mol ] % still more preferably. the content of the repeat unit expressed with general formula (XI) - (XIII) -- under [ all ] a polymer presentation -- setting -- general -- 0-70-mol % -- desirable -- 10-60-mol % -- it is used in [ 20-50 mol ] % still more preferably. the content of the repeat unit expressed with general formula (XV) - (XVII) -- under [ all ] a polymer presentation -- setting -- general -- 0-70-mol % -- desirable -- 10-60-mol % -- it is used in [ 20-50 mol ] % still more preferably.

[0090] It is still more desirable to have at least one for the repeat unit indicated to be at least one by general formula (IV)- (VI) as resin of (A) of this invention in the repeat unit shown by the general formula (I) - (III). Moreover, it is still more desirable like the above to have at least one for the repeat unit indicated to be at least one by general formula (VIII)- (X) as resin of (A) of this invention in the repeat unit shown by general formula (IV)- (VI).

[0091] Furthermore, it is still more desirable like the above to have at least one for the repeat unit indicated to be at least one by general formula (XV) - (XVII) as resin of (A) of this invention in the repeat unit shown by general formula (IV) - (VII). Thereby, the permeability of 157nm in resin can fully be raised, and the fall of dry etching-proof nature can be suppressed.

[0092] The resin of (A) of this invention the repeat unit shown by the general formula (I) - (III) At least one When it has at least one, the sum total of the content of the repeat unit shown by the general formula (I) - (III) the repeat unit shown by general formula (IV)- (VI) under [ all ] a polymer presentation -- setting -- general -- less than [ 70 mol % ] -- desirable -- 10-60-mol % -- it is used in [ 20-50 mol ] % still more preferably. the sum total of the content of

the repeat unit expressed with general formula (IV)– (VI) -- under [ all ] a polymer presentation -- setting -- general -- 10 – 80–mol % -- desirable -- 30 – 70–mol % -- it is used in [ 35 – 65 mol ] % still more preferably.

[0093] The resin of (A) of this invention the repeat unit shown by general formula (IV)– (VI) At least one When it has at least one, the sum total of the content of the repeat unit shown by general formula (IV)– (VI) the repeat unit shown by general formula (VIII)– (X) under [ all ] a polymer presentation -- setting -- general -- 10–80–mol % -- desirable -- 30–70–mol % -- it is used in [ 35–65 mol ] % still more preferably. the sum total of the content of the repeat unit expressed with general formula (VIII)– (X) -- under [ all ] a polymer presentation -- setting -- general -- less than [ 70 mol % ] -- desirable -- 10 – 60–mol % -- it is used in [ 20 – 50 mol ] % still more preferably.

[0094] The resin of (A) of this invention the repeat unit shown by general formula (IV) – (VII) At least one When it has at least one, the sum total of the content of the repeat unit shown by general formula (IV) – (VII) the repeat unit shown by general formula (XV) – (XVII) under [ all ] a polymer presentation -- setting -- general -- 10–80–mol % -- desirable -- 30–70–mol % -- it is used in [ 35–65 mol ] % still more preferably. the sum total of the content of the repeat unit expressed with general formula (XV) – (XVII) -- under [ all ] a polymer presentation -- setting -- general -- less than [ 70 mol % ] -- desirable -- 10–60–mol % -- it is used in [ 20–50 mol ] % still more preferably.

[0095] a general formula (IA) and (IIA) the repeat unit shown -- each -- the content of the repeat unit shown by the general formula (IA) in the fluorine radical content resin (A) which it has one even if few -- under [ all ] a polymer presentation -- general -- 5 – 80–mol % -- desirable -- 10 – 75–mol % -- it is 20 – 70–mol % still more preferably. a general formula (IA) and (IIA) the repeat unit shown -- each -- the content of the repeat unit shown by the general formula (IIA) in the fluorine radical content resin (A) which it has one even if few -- under [ all ] a polymer presentation -- general -- 5 – 80–mol % -- desirable -- 10 – 70–mol % -- it is 20 – 65–mol % still more preferably. a general formula (IIA) and (VIA) the repeat unit shown -- each -- the content of the repeat unit shown by the general formula (IIA) in the fluorine radical content resin (A) which it has one even if few -- under [ all ] a polymer presentation -- general -- 5 – 80–mol % -- desirable -- 10 – 70–mol % -- it is 20 – 65–mol % still more preferably. a general formula (IIA) and (VIA) the repeat unit shown -- each -- the content of the repeat unit shown by the general formula (VIA) in the fluorine radical content resin (A) which it has one even if few -- under [ all ] a polymer presentation -- general -- 5 – 80–mol % -- desirable -- 10 – 70–mol % -- it is 20 – 65–mol % still more preferably. the content of the repeat unit shown by the general formula (IIIA) in these fluorine radical content resin (A) -- under [ all ] a polymer presentation -- general -- 1 – 40–mol % -- desirable -- 3 – 35–mol % -- it is 5 – 30–mol % still more preferably. the content of the repeat unit shown by the general formula (VIIA) in these fluorine radical content resin (A) -- under [ all ] a polymer presentation -- general -- 1 – 40–mol % -- desirable -- 3 – 35–mol % -- it is 5 – 30–mol % still more preferably.

[0096] Besides the above repeat structural units, the resin of this invention (A) is the purpose which raises the engine performance of the positive resist of this invention further, and may carry out copolymerization of other polymerization nature monomers.

[0097] What is shown below is contained as a copolymerization monomer which can be used. For example, it is the compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester other than the above, acrylamides, methacrylic ester, methacrylamide, an allyl compound, vinyl ether, vinyl ester, styrene, and crotonic-acid ester.

[0098] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic-acid propyl -- Acrylic-acid t-butyl, acrylic-acid amyl, acrylic-acid cyclohexyl, Acrylic-acid ethylhexyl, acrylic-acid octyl, acrylic-acid-t-octyl, Chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, Aryl acrylate (for example, phenyl acrylate etc.), such as pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, furfuryl acrylate, and tetrahydrofurfuryl acrylate;

[0099] Methacrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10) methacrylate for example, methyl methacrylate, ethyl methacrylate, and propyl methacrylate -- Isopropyl methacrylate, t-butyl methacrylate, amyl methacrylate, Hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2 and 2-dimethyl-3-hydroxypropyl methacrylate, trimethylol propane mono-methacrylate, Pentaerythritol mono-methacrylate, glycidyl methacrylate, Aryl methacrylate (for example, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, etc.), such as furfuryl methacrylate and tetrahydrofurfuryl methacrylate;

[0100] Acrylamides, for example, acrylamide, N-alkyl acrylamide (as an alkyl group), there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, benzyl, a hydroxyethyl radical, etc. N-aryl acrylamide (as an aryl group, there are a phenyl group, a tolyl group, a nitrophenyl group, a naphthyl group, a cyanophenyl radical, a hydroxyphenyl radical, a carboxyphenyl radical, etc., for example.) N and N-dialkyl acrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc. N and N-diaryl acrylamide (as an aryl group, there is a phenyl group etc., for example.) N-methyl-N-phenyl acrylamide, N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0101] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, t-butyl, an ethylhexyl radical, a hydroxyethyl radical, a cyclohexyl radical, etc. N-aryl methacrylamide (there is a phenyl group etc. as an aryl group.) N and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group.) N and N-diaryl methacrylamide (there is a phenyl group etc. as an aryl group.) N-hydroxyethyl-N-methyl methacrylamide, N-methyl-N-phenyl methacrylamide, N-ethyl-N-phenyl methacrylamide etc.; An allyl compound For example, allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.;

[0102] vinyl ether (for example, hexyl vinyl ether --), for example, alkyl vinyl ether Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, Dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, Butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc., Vinyl aryl ether (for example, vinyl phenyl ether, the vinyl

tolyl ether, vinyl KURORU phenyl ether, vinyl -2, 4-dichloro phenyl ether, the vinyl naphthyl ether, the vinyl anthranil ether, etc.);

[0103] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, Vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, Vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, Vinyl methoxy acetate, vinyl butoxy acetate, vinyl phenyl acetate, Vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, benzoic-acid vinyl, salicylic acid vinyl, Krol benzoic-acid vinyl, tetra-KURORU benzoic-acid vinyl, naphthoic-acid vinyl, etc.;

[0104] styrene, for example, styrene, and alkyl styrene (for example, methyl styrene --) Dimethyl styrene, trimethyl styrene, ethyl styrene, diethyl styrene, Isopropyl styrene, butyl styrene, hexyl styrene, cyclohexyl styrene, DESHIRU styrene, benzyl styrene, KURORU methyl styrene, trifluormethyl styrene, Alkoxy styrene, such as ethoxy methyl styrene and acetoxy methyl styrene for example, methoxy styrene and 4-methoxy-3-methyl styrene -- halogen styrene (for example, KURORU styrene --), such as dimethoxy styrene Dichloro styrene, TORIKURORU styrene, tetra-KURORU styrene, pen TAKURORU styrene, bromine styrene and a jib -- carboxy styrene, such as ROM styrene, iodine styrene, Fluor styrene, Tori Fluor styrene, 2-bromine-4-trifluormethyl styrene, and 4-Fluor-3-trifluormethyl styrene, and vinyl naphthalene;

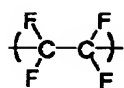
[0105] Crotonic-acid ester (for example, dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc.), for example, crotonic-acid alkyl (for example, crotonic-acid butyl, crotonic-acid hexyl, glycerol mono-crotonate, etc.); itaconic-acid dialkyls,; there are the dialkyl ester of a maleic acid or boletic acid, maleic anhydrides (for example, dimethyl MARERETO, dibutylfumarate, etc.), maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc. In addition, generally what is necessary is just a copolymerizable addition polymerization nature unsaturated compound.

[0106] Although the example of the repeat structural unit expressed with general formula (I) - (X) below is shown, this invention is not limited to this.

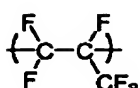
[0107]

[Formula 17]

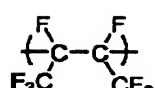




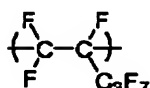
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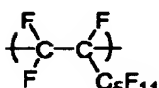
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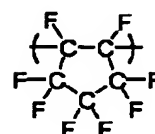
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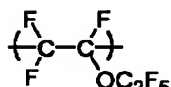
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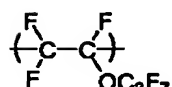
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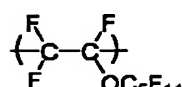
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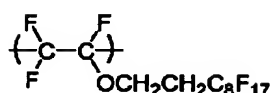
(F-7)



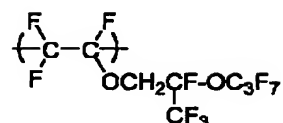
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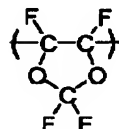
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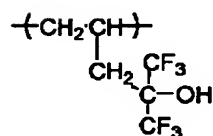
( F-10 )



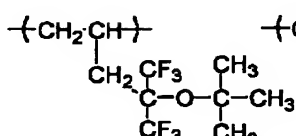
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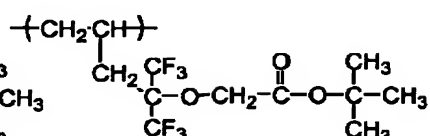
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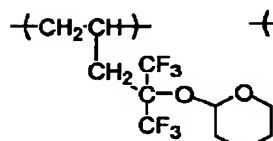
( F-13 )



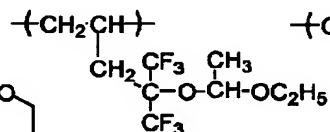
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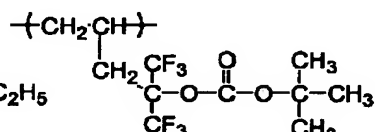
( F-15 )



(F-16)



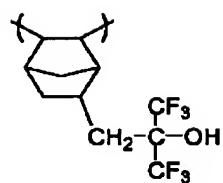
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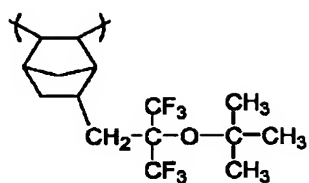
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[0108]

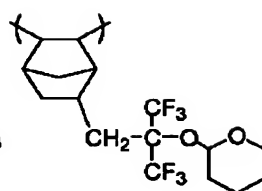
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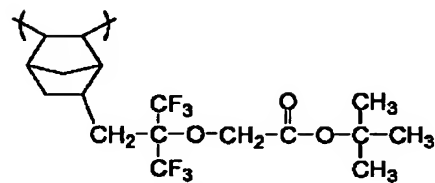
(F-19)



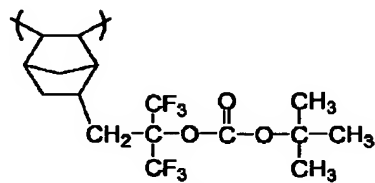
(F-20)



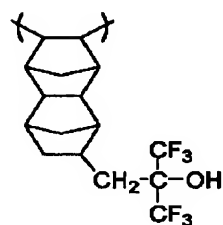
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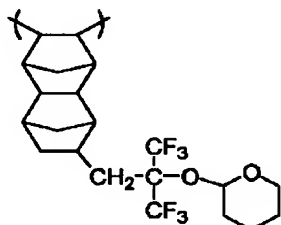
(F-22)



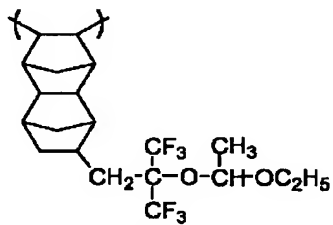
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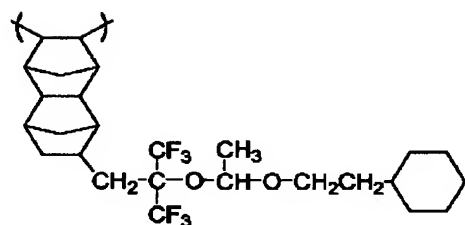
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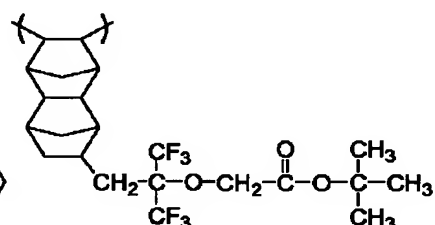
(F-25)



(F-26)



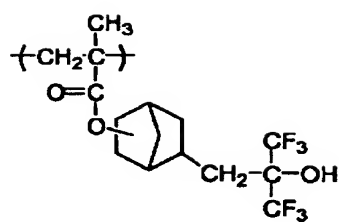
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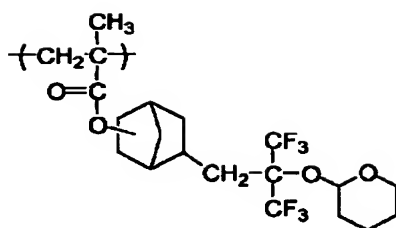
(F-28)

[0109]

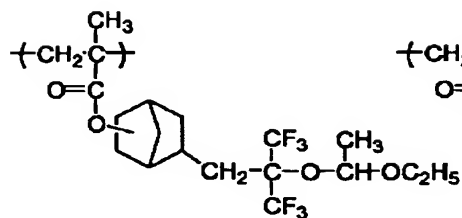
[Formula 19]



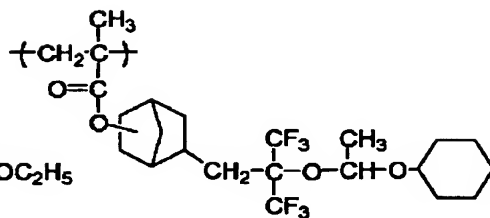
(F-29)



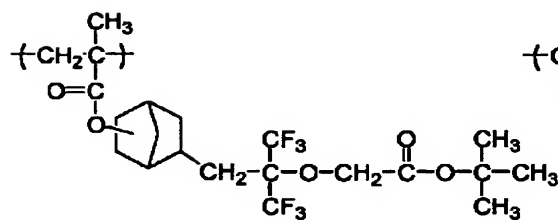
(F-30)



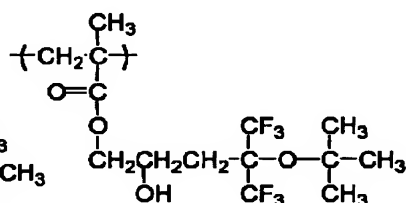
(F-31)



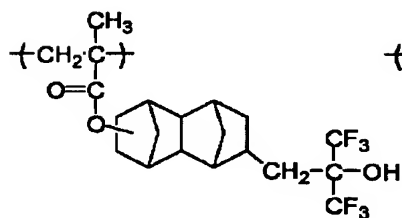
(F-32)



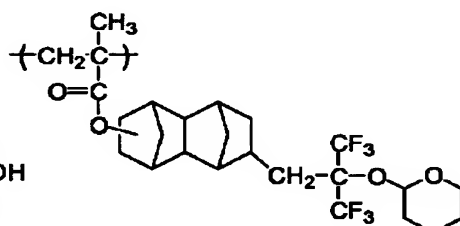
(F-33)



(F-34)



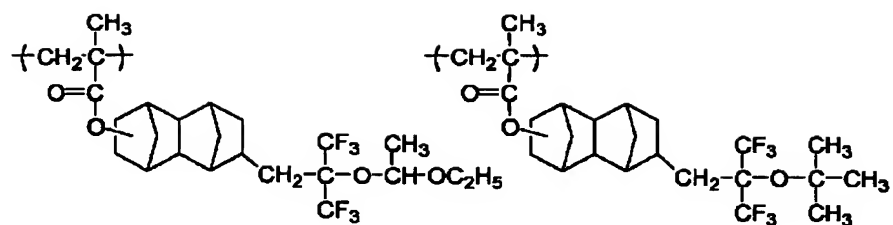
(F-35)



(F-36)

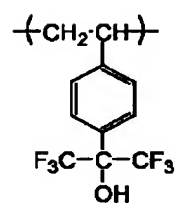
[0110]

[Formula 20]

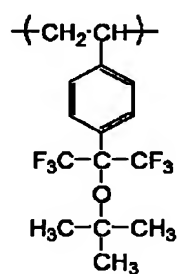


(F-37)

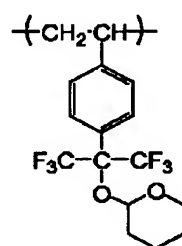
(F-38)



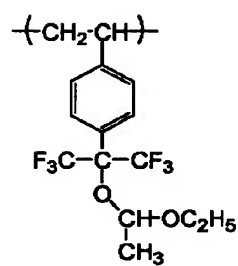
(F-39)



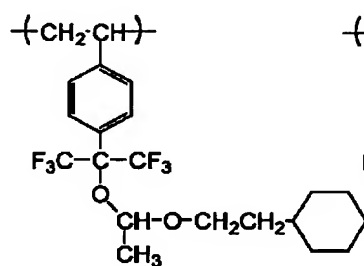
(F-40)



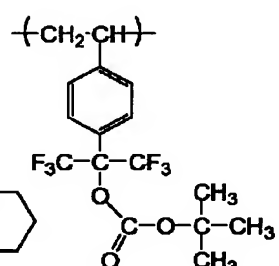
(F-41)



(F-42)



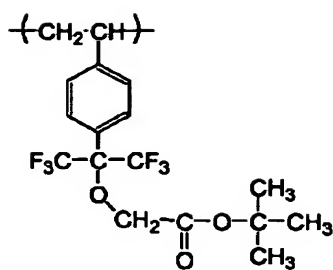
(F-43)



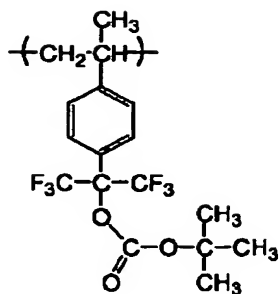
(F-44)

[0111]

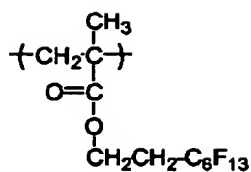
[Formula 21]



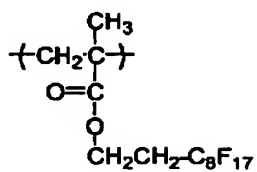
(F-45)



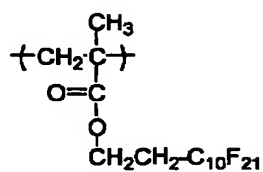
(F-46)



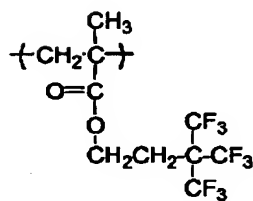
(F-47)



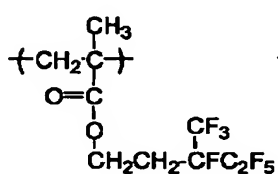
(F-48)



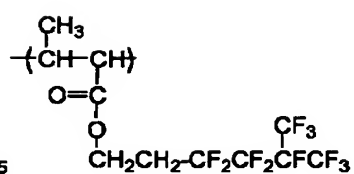
(F-49)



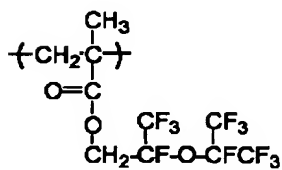
(F-50)



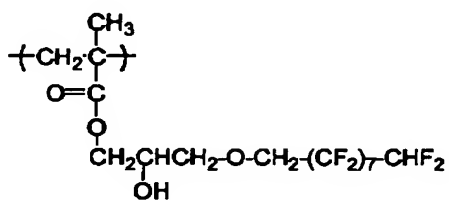
(F-51)



(F-52)



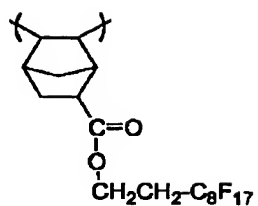
(F-53)



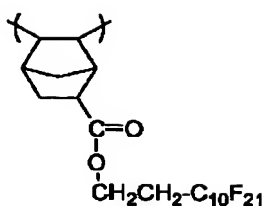
(F-54)

[0112]

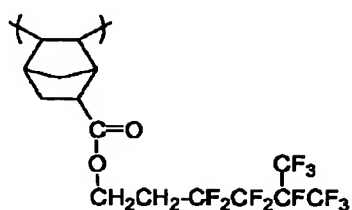
[Formula 22]



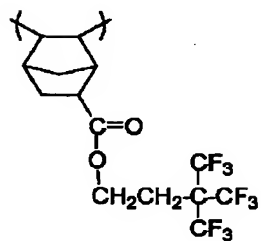
(F-55)



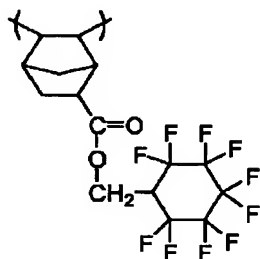
(F-56)



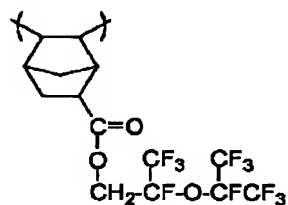
(F-57)



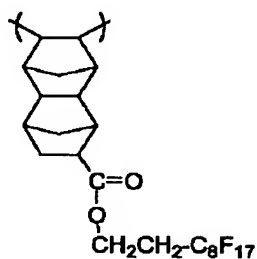
(F-58)



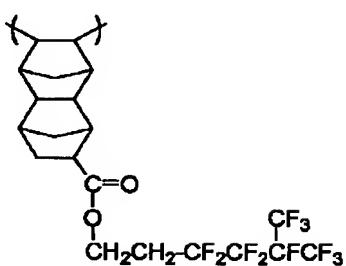
(F-59)



(F-60)



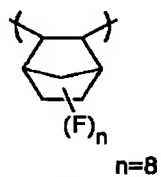
(F-61)



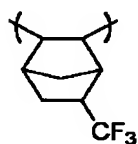
(F-62)

[0113]

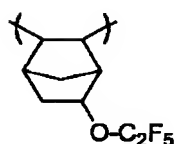
[Formula 23]



(F-63)



(F-64)

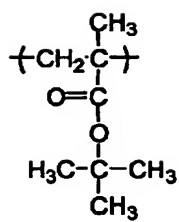


(F-65)

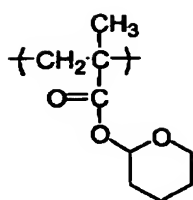
[0114] Moreover, although the example of the repeat structural unit expressed with general formula (XI) – (XIII) is shown, this invention is not limited to this.

[0115]

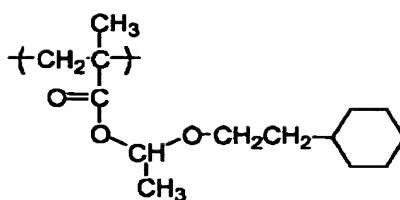
[Formula 24]



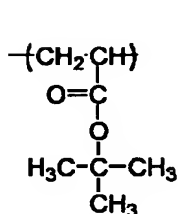
(B-1)



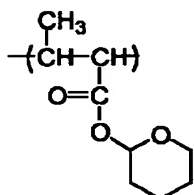
(B-2)



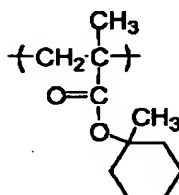
(B-3)



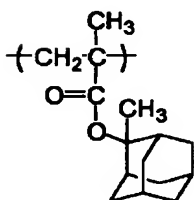
(B-4)



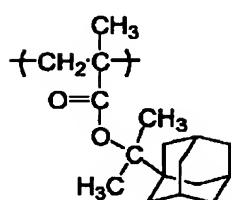
(B-5)



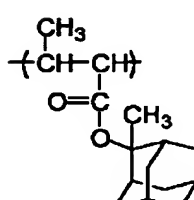
(B-6)



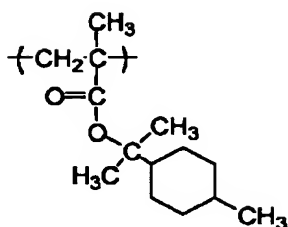
(B-7)



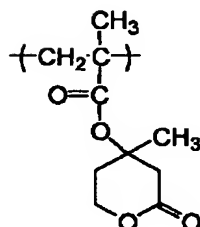
(B-8)



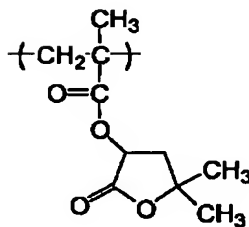
(B-9)



(B-10)



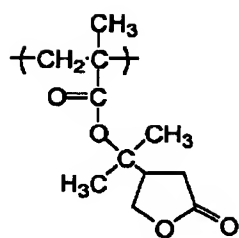
(B-11)



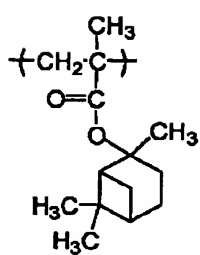
(B-12)

[0116]

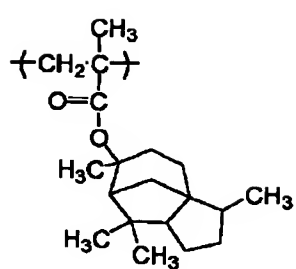
[Formula 25]



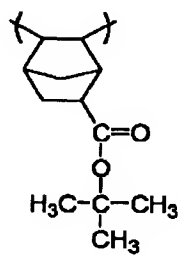
(B-13)



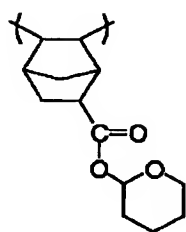
(B-14)



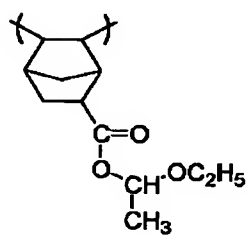
(B-15)



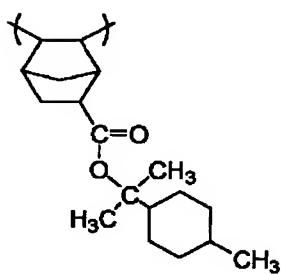
(B-16)



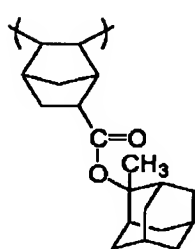
(B-17)



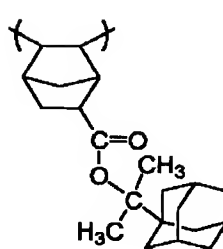
(B-18)



(B-19)



(B-20)

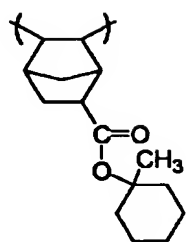


(B-21)

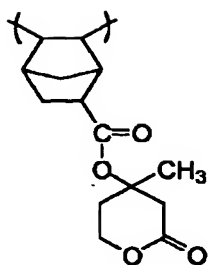
[0117]

[Formula 26]

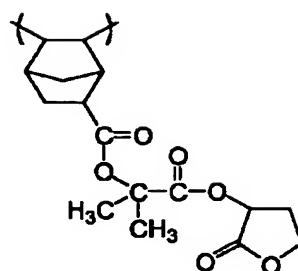




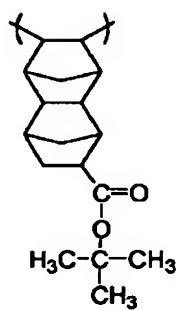
( B-22 )



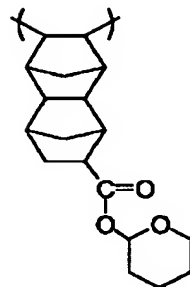
( B-23 )



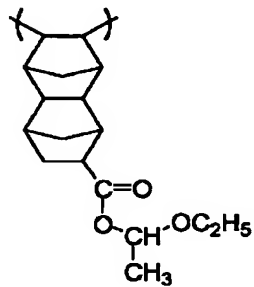
( B-24 )



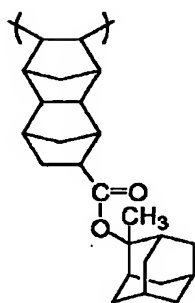
( B-25 )



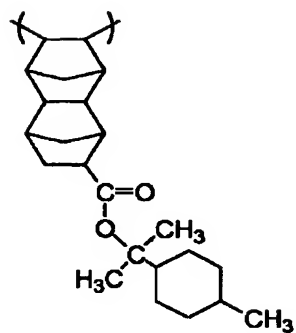
( B-26 )



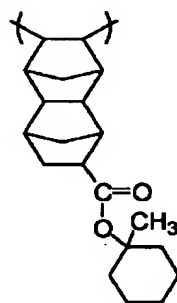
( B-27 )



( B-28 )



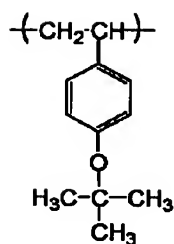
( B-29 )



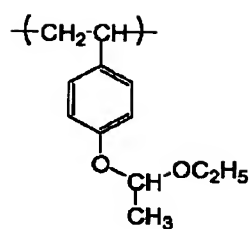
( B-30 )

[0118]

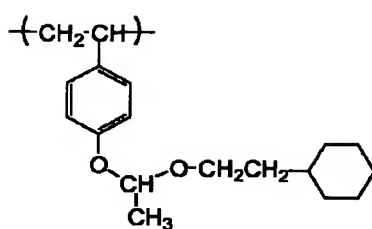
[Formula 27]



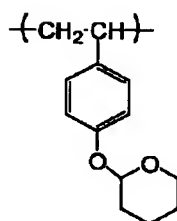
(B-31)



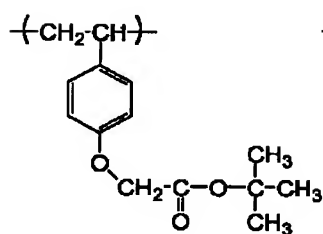
(B-32)



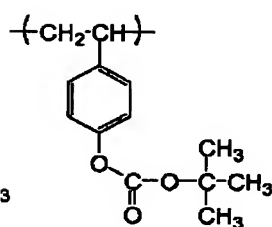
(B-33)



(B-34)



(B-35)

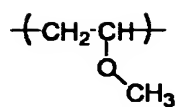


(B-36)

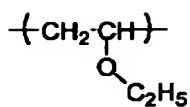
[0119] Moreover, although the example of the repeat structural unit expressed with general formula (XVI) – (XVII) is shown, this invention is not limited to this.

[0120]

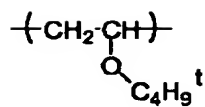
[Formula 28]



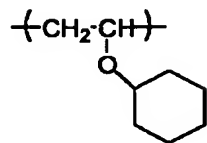
(C-1)



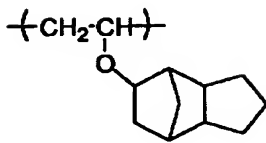
(C-2)



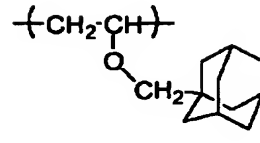
(C-3)



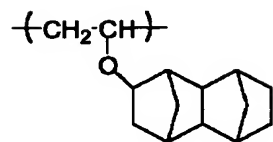
(C-4)



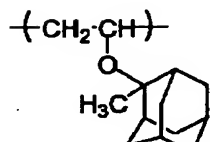
(C-5)



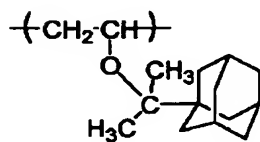
(C-6)



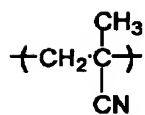
(C-7)



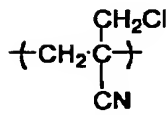
(C-8)



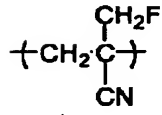
(C-9)



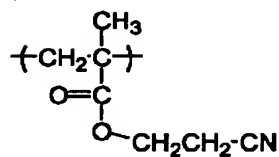
(C-10)



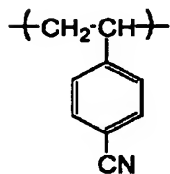
(C-11)



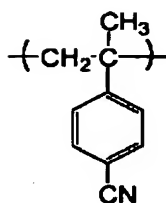
(C-12)



(C-13)



(C-14)

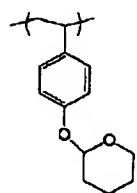


(C-15)

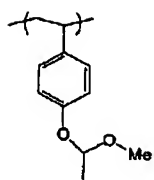
[0121] Although the example of the repeat structural unit expressed with a general formula (IA) below is shown, this invention is not limited to this.

[0122]

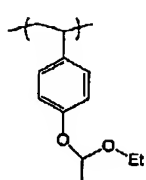
[Formula 29]



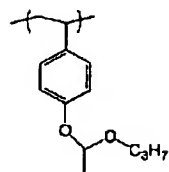
(A-1)



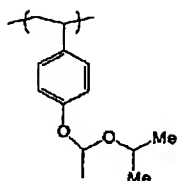
(A-2)



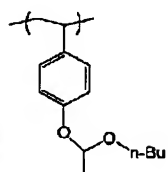
(A-3)



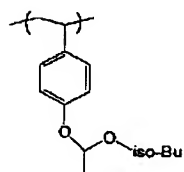
(A-4)



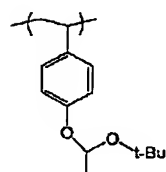
(A-5)



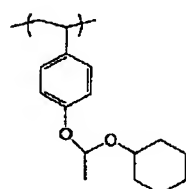
(A-6)



(A-7)



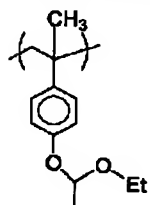
(A-8)



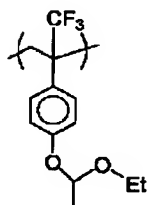
(A-9)

[0123]

[Formula 30]



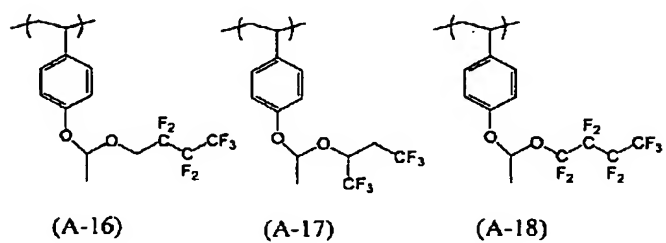
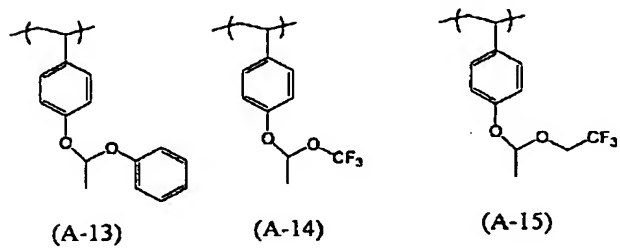
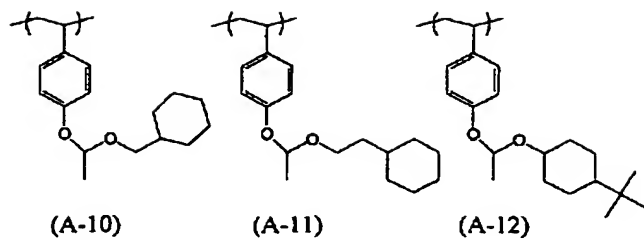
(A-3' )



(A-3'')

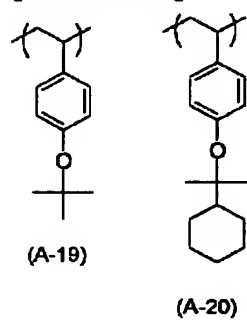
[0124]

[Formula 31]



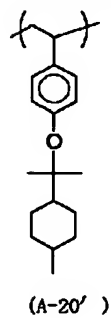
[0125]

[Formula 32]



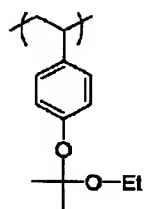
[0126]

[Formula 33]



[0127]

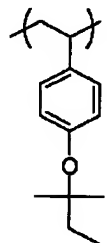
[Formula 34]



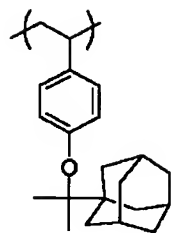
(A-24)

[0128]

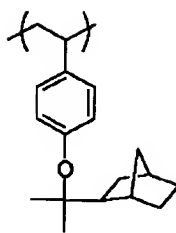
[Formula 35]



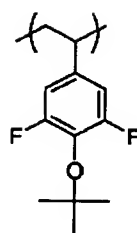
(A-25)



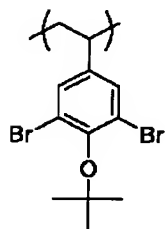
(A-26)



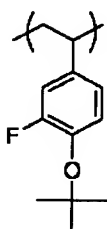
(A-27)



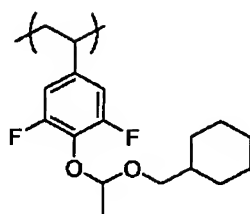
(A-28)



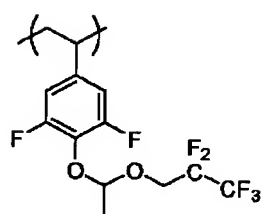
(A-29)



(A-30)



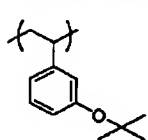
(A-31)



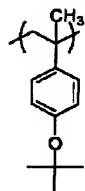
(A-32)

[0129]

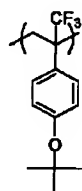
[Formula 36]



(A-33)



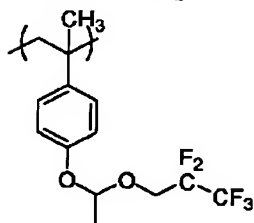
(A-34)



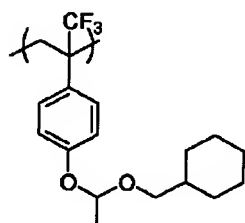
(A-35)

[0130]

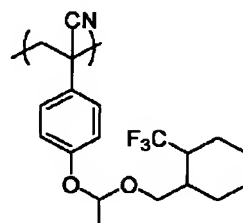
[Formula 37]



(A-37)



(A-38)

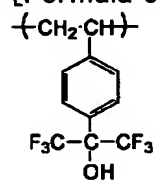


(A-39)

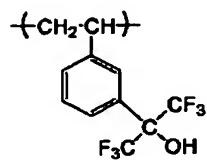
[0131] Although the example of the repeat structural unit expressed with a general formula (IIA) below is shown, this invention is not limited to this.

[0132]

[Formula 38]



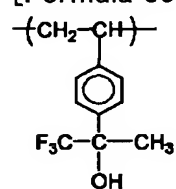
(II-1)



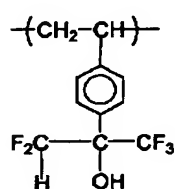
(II-2)

[0133]

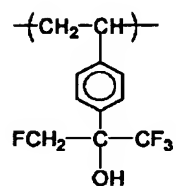
[Formula 39]



(II-1')



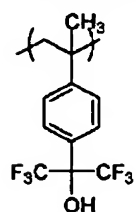
(II-1'')



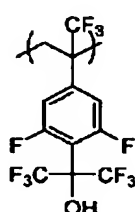
(II-1''')

[0134]

[Formula 40]



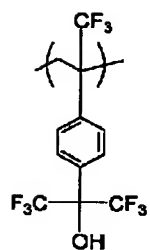
(II-3)



(II-4)

[0135]

[Formula 41]



(II-3')

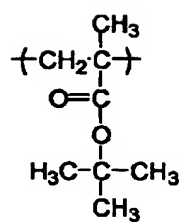
[0136] Furthermore, - (F-40) (F-45) illustrated previously can be mentioned as an example of the repeat unit expressed with a general formula (IIA).

[0137] Although the example of the repeat structural unit expressed with a general formula (VIA) below is shown, this invention is not limited to these.

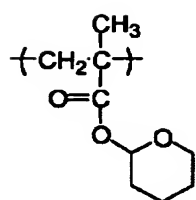
[0138]

[Formula 42]

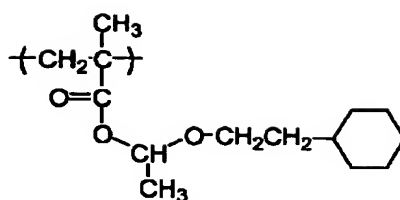




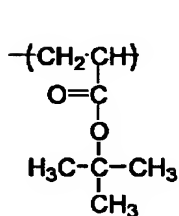
(B-1)



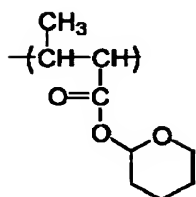
(B-2)



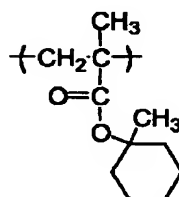
(B-3)



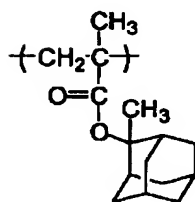
(B-4)



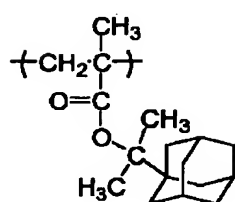
(B-5)



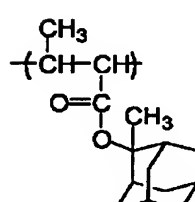
(B-6)



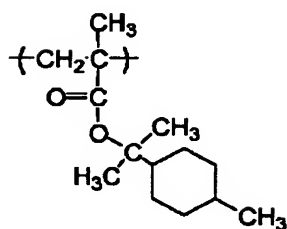
(B-7)



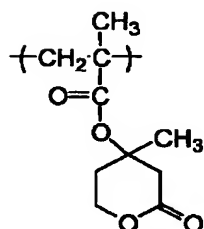
(B-8)



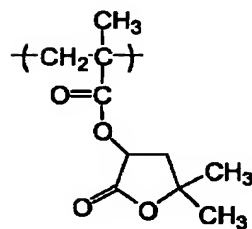
(B-9)



(B-10)



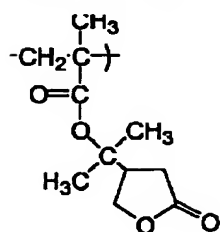
(B-11)



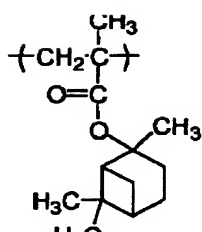
(B-12)

[0139]

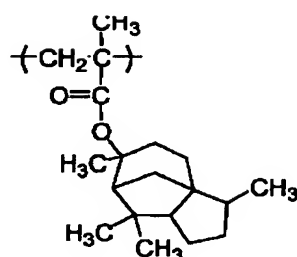
[Formula 43]



(B-13)



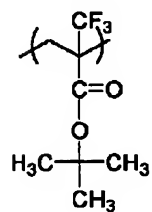
(B-14)



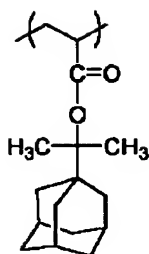
(B-15)

[0140]

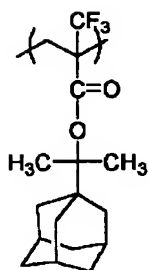
[Formula 44]



(B-1')



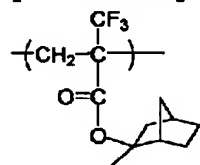
(B-8')



(B-8'')

[0141]

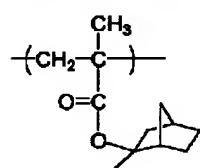
[Formula 45]



(B-12' )

[0142]

[Formula 46]



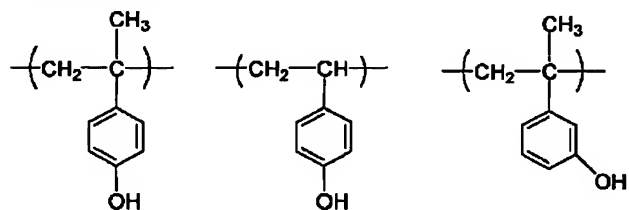
(B-12'')

[0143] Furthermore, - (F-29) (F-38) and (F-47) - (F-54) which were previously illustrated as an example of the repeat unit expressed with a general formula (VIA) can be mentioned.

[0144] Although the example of the repeat structural unit expressed with a general formula (IIIA) below is shown, this invention is not limited to this.

[0145]

[Formula 47]



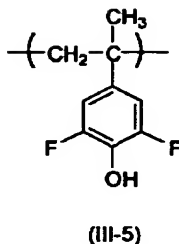
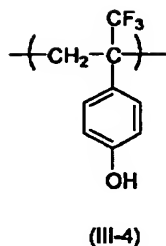
(III-1)

(III-2)

(III-3)

[0146]

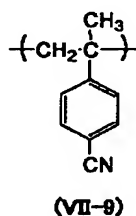
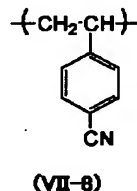
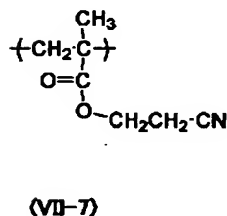
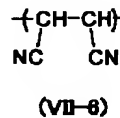
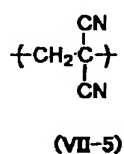
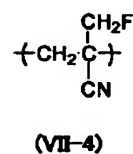
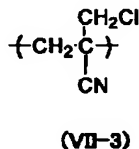
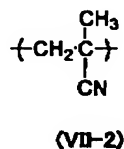
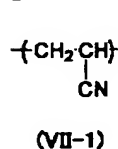
[Formula 48]



[0147] Although the example of the repeat structural unit expressed with a general formula (VIIA) below is shown, this invention is not limited to this.

[0148]

[Formula 49]



[0149] The repeat structural unit expressed with the above-mentioned example may be respectively used by one sort, and plurality may be mixed and used for it. The desirable molecular weight of the resin (A) of this invention which has the above-mentioned repeat structural unit is 1,000-200,000 in a weighted mean, and is used in 3,000-20,000 still more preferably. molecular weight distribution -- 1-10 -- it is -- desirable -- 1-3 -- the thing of the range of 1-2 is used still more preferably. The smaller thing of a molecular weight distribution has resolution, a resist configuration, and the more smooth side attachment wall of a resist pattern, and is excellent in the Rhine edge roughness nature.

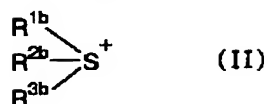
[0150] Generally the addition of the resin (A) of this invention is preferably used in 65 - 95% of the weight of the range still more preferably 60 to 98% of the weight 50% of the weight or more on the basis of the total solids of a constituent.

[0151] The acid generator used by acid generator this invention which generates an acid by the exposure of [2] (B) activity beam of light or a radiation is a compound (henceforth "(B) component" or an "acid generator") which has the sulfonium salt which generates an acid by the exposure of an activity beam of light or a radiation, and which does not have a ring, or phenacyl sulfonium salt structure.

[0152] The sulfonium salt which does not have a ring is a salt which makes a cation the sulfonium expressed with a degree type (II).

[0153]

[Formula 50]

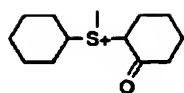


[0154] R1 b-R3b expresses respectively the organic radical which does not contain a ring independently among a formula. A ring also includes the aromatic series ring containing a hetero atom here. the organic radical which does not contain the ring as R1b-R3b -- general -- carbon numbers 1-30 -- they are carbon numbers 1-20 preferably. R1 b-R3b -- each -- independent -- desirable -- an alkyl group, a 2-oxo-alkyl group, an alkoxy carbonylmethyl radical, an allyl group, and a vinyl group -- it is -- further -- desirable -- a straight chain, branching, an annular 2-oxo-alkyl group, and an alkoxy carbonylmethyl radical -- they are a straight chain and a branching 2-oxo-alkyl group most preferably. The alkyl groups as R1b-R3b may be a straight chain, branching, and annular any, and can mention the straight chain of carbon numbers 1-10 or a branching alkyl group (for example, a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical), and the annular alkyl group (a cyclopentyl group, a cyclohexyl radical, norbornyl radical) of carbon numbers 3-10 preferably. The 2-oxo-alkyl groups as R1b-R3b may be a straight chain, branching, and annular any, and can mention preferably the radical which has >C=O in the 2nd place of the above-mentioned alkyl group. As an alkoxy group in the alkoxy carbonylmethyl radical as R1b-R3b, the alkoxy group (a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, pentoxy radical) of carbon numbers 1-5 can be mentioned preferably. R1 b-R3b may be further permuted by a halogen atom, the alkoxy group (for example, carbon numbers 1-5), the hydroxyl group, the cyano group, and the nitro group. Two of R1 b-R3b may join together, a ring structure may be formed, and an oxygen atom, a sulfur atom, an ester bond, amide association, and a carbonyl group may be included in endocyclic. As a radical which two of R1 b-R3b combine and form, an alkylene group (for example, a butylene radical, a pentene radical) can be mentioned. The radical on which any one of R1 b-R3b has carbon-carbon duplex association or carbon-oxygen duplex association from a viewpoint of photoreaction nature is desirable. As an anion of the sulfonium salt which does not have a ring, it is a sulfonic-acid anion, and it is benzenesulfonic acid preferably permuted with the alkane sulfonic-acid anion and electronic suction nature machine by which the 1st place was permuted with the fluorine atom, and is the perphloro alkane sulfonic-acid anion of carbon numbers 1-8 still more preferably, and they are a perphloro butane sulfonic-acid anion and a perphloro octane sulfonic-acid anion most preferably. \*\*\*\* for these -- the catabolic rate of an acidolysis nature machine improves by things, and sensibility is excellent, and the diffusibility of a generating acid is controlled, and resolution improves. In addition, as an electronic suction nature machine, a fluorine atom, a chlorine atom, a bromine atom, a nitro group, a cyano group, an alkoxy carbonyl group, an acyloxy radical, an acyl group, etc. can be mentioned. It is very good in the structure which at least one of the R1 b-R3b of a compound expressed with a general formula (II) combines with at least one of the R1 b-R3b of other compounds expressed with a general formula (II).

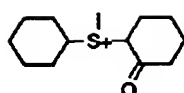
[0155] Although the example of sulfonium salt in which it does not have the ring which can be used for below by this invention is shown, this invention is not limited to these.

[0156]

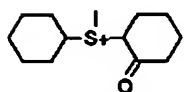
[Formula 51]



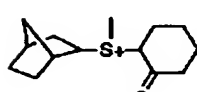
$\text{CF}_3\text{SO}_3^-$   
(II-1)



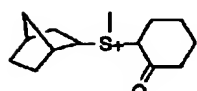
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-2)



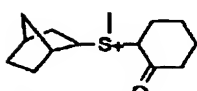
$\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$   
(II-3)



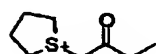
$\text{CF}_3\text{SO}_3^-$   
(II-4)



$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-5)



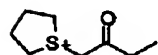
$\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$   
(II-6)



$\text{CF}_3\text{SO}_3^-$   
(II-7)



$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-8)



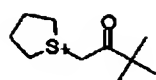
$\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$   
(II-9)



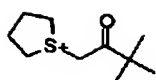
$\text{CF}_3\text{SO}_3^-$   
(II-10)

[0157]

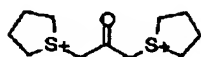
[Formula 52]



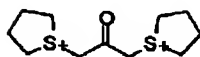
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-11)



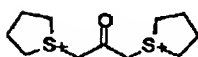
$\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$   
(II-12)



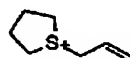
2  $\text{CF}_3\text{SO}_3^-$   
(II-13)



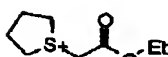
2  $\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-14)



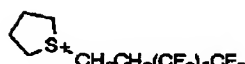
2  $\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$   
(II-15)



$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-16)



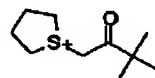
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-17)



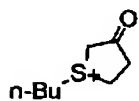
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-18)



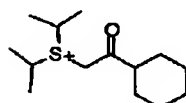
$\text{CF}_3\text{CF}_2\text{O-CF}_2\text{CF}_2\text{SO}_3^-$   
(II-19)



$\text{CF}_3\text{CF}_2\text{O-CF}_2\text{CF}_2\text{SO}_3^-$   
(II-20)



$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-21)

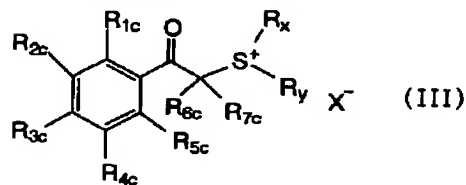


$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$   
(II-22)

[0158] The compound expressed in the following general formulas (III) as the compound which generates an acid by the exposure of an activity beam of light or a radiation, and which has phenacyl sulfonium salt structure can be mentioned.

[0159]

[Formula 53]



[0160] R1 c-R5c expresses a hydrogen atom, an alkyl group, an alkoxy group, or a halogen atom independently respectively. R6c and R7c express a hydrogen atom, an alkyl group, or an aryl group independently respectively. Rx and Ry express an alkyl group, a 2-oxo-alkyl group, an

alkoxy carbonylmethyl radical, an allyl group, or a vinyl group independently respectively. It may join together, respectively, any two or more of R1 c-R7c, and Rx and Ry may form a ring structure, and this ring structure may include an oxygen atom, a sulfur atom, an ester bond, and amide association. X- expresses the anion of a sulfonic acid, a carboxylic acid, or sulfonylimide.

[0161] the alkyl group as R1c-R5c -- a straight chain, branching, and annular any -- you may be -- for example, the alkyl group of carbon numbers 1-10 -- the straight chain of carbon numbers 1-5 and a branching alkyl group (for example, a methyl group, an ethyl group, a straight chain or a branching propyl group, a straight chain or branching butyl, a straight chain, or a branching pentyl radical), and the annular alkyl group (for example, a cyclopentyl group, a cyclohexyl radical) of carbon numbers 3-8 can be mentioned preferably. the alkoxy group as R1c-R5c -- a straight chain, branching, and annular any -- you may be -- for example, the alkoxy group of carbon numbers 1-10 -- the straight chain of carbon numbers 1-5 and a branching alkoxy group (for example, a methoxy group, an ethoxy radical, a straight chain or a branching propoxy group, a straight chain or a branching butoxy radical, a straight chain, or a branching pentoxy radical), and the annular alkoxy group (for example, a cyclopenthyloxy radical, a cyclohexyloxy radical) of carbon numbers 3-8 can be mentioned preferably. Either is a straight chain, branching, an annular alkyl group or a straight chain, branching, and an annular alkoxy group among R1 c-R5c preferably, and the sums of the carbon number of R1c to R5c are 2-15 still more preferably. Thereby, solvent solubility improves more and generating of particle is controlled at the time of preservation of a resist constituent.

[0162] About an alkyl group, the same thing as the alkyl group as R1c-R5c can be mentioned as R6c and R7c. As an aryl group, the aryl group (for example, phenyl group) of carbon numbers 6-14 can be mentioned, for example. The alkyl group as Rx and Ry can mention the same thing as the alkyl group as R1c-R5c. A 2-oxo-alkyl group can mention the radical which has  $>C=O$  to the 2nd place of the alkyl group as R1c-R5c. About the alkoxy group in an alkoxy carbonylmethyl radical, the same thing as the alkoxy group as R1c-R5c can be mentioned. A butylene radical, a pentene radical, etc. can be mentioned as a radical which Rx and Ry combine and form.

[0163] By forming a ring, a spacial configuration is fixed and photolysis ability of the compound of a formula (III) improves. About the case where any two of R1 c-R7c join together, and a ring structure is formed The case where any one of any one of the R1 c-R5c, R6c, and the R7c joins together, become single bond or a connection radical, and a ring is formed is desirable, and the case where R5c, R6c, or R7c joins together especially, become single bond or a connection radical, and a ring is formed is desirable. The alkylene group and the alkylene group containing an oxygen atom which can mention the radical which comes to combine the alkylene group which may have the substituent, the alkenylene group which may have the substituent, -O-, -S-, -CO-, -CONR- (for R to be a hydrogen atom, an alkyl group, and an acyl group), and these [ two / or more ] as a connection radical, and may have the substituent further, and the alkylene group containing a sulfur atom are desirable. As a substituent, an alkyl group (preferably carbon numbers 1-5), an aryl group, preferably carbon numbers 6-10, for example, a phenyl group, an acyl group (for example, carbon numbers 2-11), etc. can be mentioned. Moreover, the connection radical which forms five to 7 membered-ring like a methylene group, ethylene, a propylene radical, -CH<sub>2</sub>-O-, and -CH<sub>2</sub>-S- is desirable, and especially the connection radical that forms six membered-rings like ethylene, -CH<sub>2</sub>-O-, and -CH<sub>2</sub>-S- is desirable. By forming six membered-rings, a carbonyl flat surface and a C-S<sup>+</sup> sigma bond become more close to a perpendicular, and photolysis ability improves by the orbital interaction.

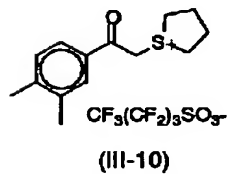
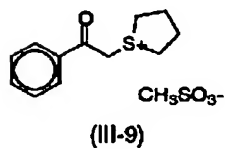
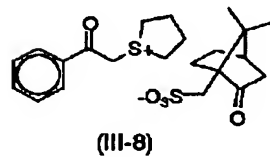
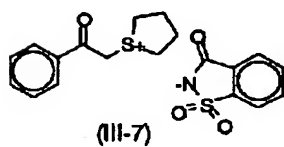
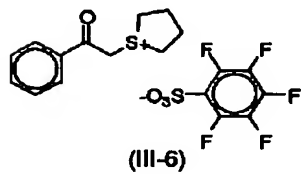
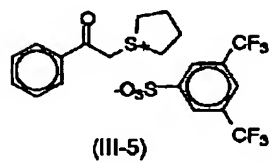
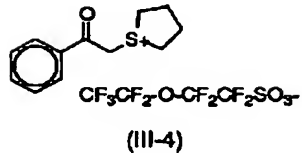
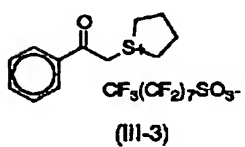
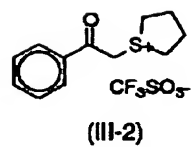
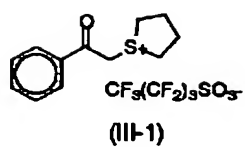
Moreover, you may be the compound which joins together through single bond or a connection radical, and has two or more structures of a formula (III) in the location of either R1c-R7c, and Rx and Ry.

[0164] X<sup>-</sup> is a sulfonic-acid anion preferably and is benzenesulfonic acid permuted with the alkane sulfonic-acid anion by which the 1st place was more preferably permuted with the fluorine atom, or the electronic suction nature machine. The alkane part of an alkane sulfonic-acid anion may be permuted by substituents, such as an alkoxy group (for example, carbon numbers 1-8) and a perfluoro alkoxy group (for example, carbon numbers 1-8). Moreover, as an electronic suction nature machine, a fluorine atom, a chlorine atom, a bromine atom, a nitro group, a cyano group, an alkoxy carbonyl group, an acyloxy radical, an acyl group, etc. can be mentioned. X<sup>-</sup> further -- desirable -- the perphloro alkane sulfonic-acid anion of carbon numbers 1-8 -- it is -- especially -- desirable -- a perphloro octane sulfonic-acid anion, a perphloro butane sulfonic-acid anion, and a truffe ROROME tongue sulfonic-acid anion -- they are a perphloro butane sulfonic-acid anion and a truffe ROROME tongue sulfonic-acid anion most preferably. \*\*\*\* for these -- the catabolic rate of an acidolysis nature machine improves by things, and sensibility is excellent, and the diffusibility of a generating acid is controlled, and resolution improves. Although the example of a compound of having the phenacyl sulfonium salt structure which can be used for below by this invention is shown, this invention is not limited to these.

[0165]

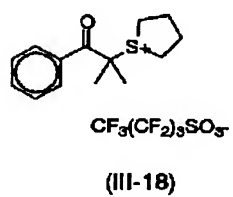
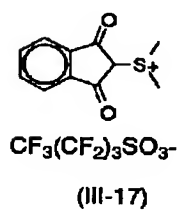
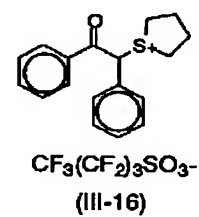
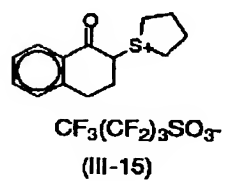
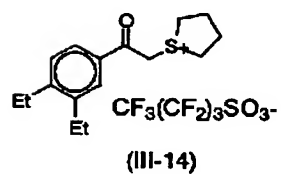
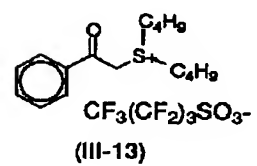
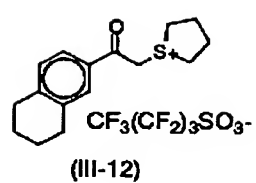
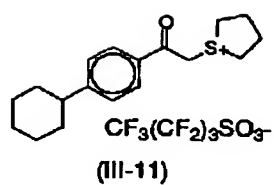
[Formula 54]





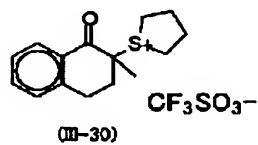
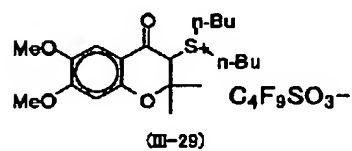
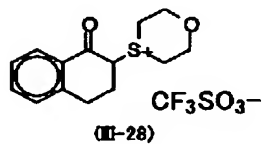
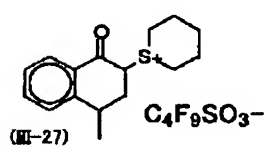
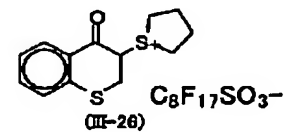
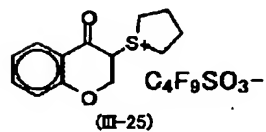
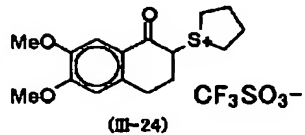
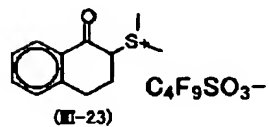
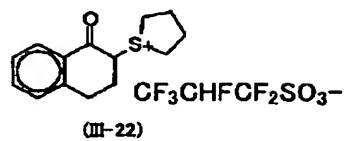
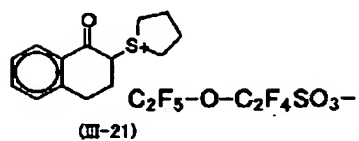
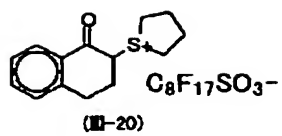
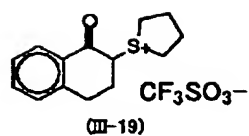
[0166]

[Formula 55]



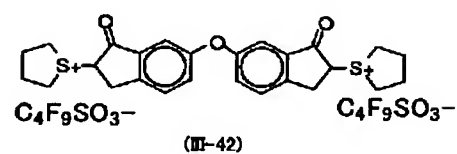
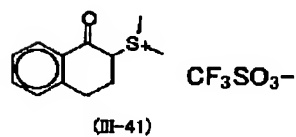
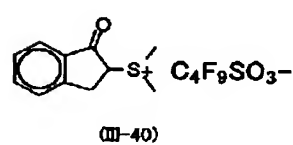
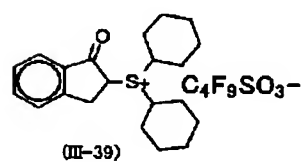
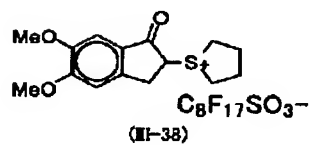
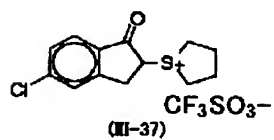
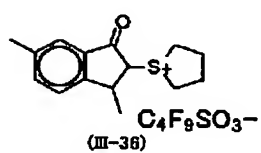
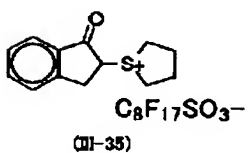
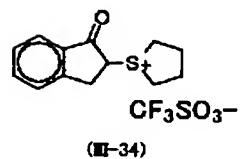
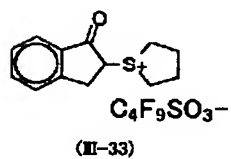
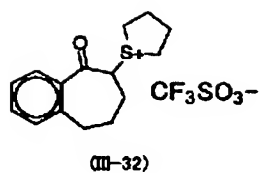
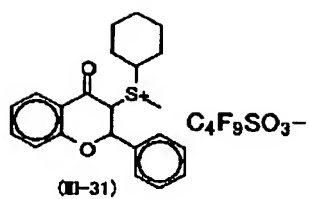
[0167]

[Formula 56]



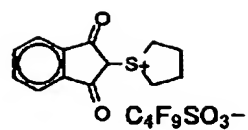
[0168]

[Formula 57]

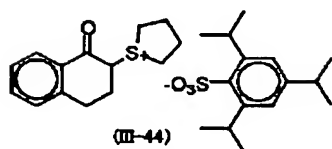


[0169]

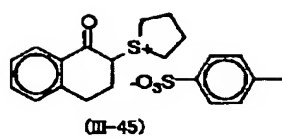
[Formula 58]



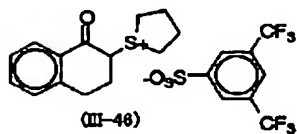
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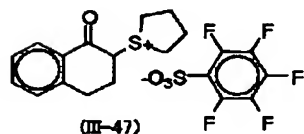
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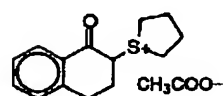
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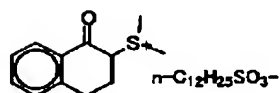
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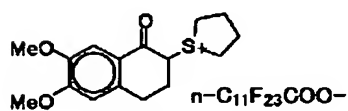
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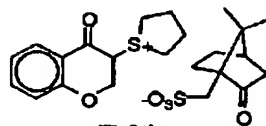
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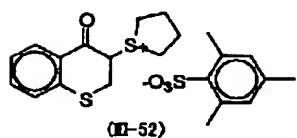
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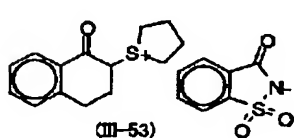
(III-50)



(III-51)



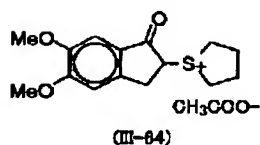
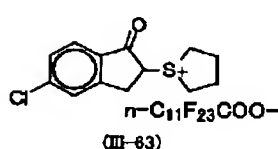
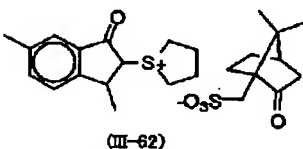
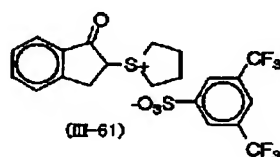
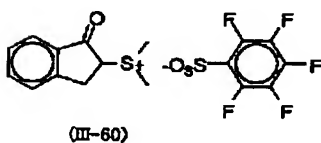
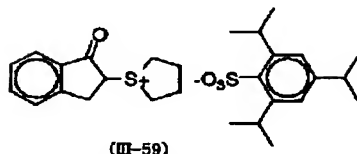
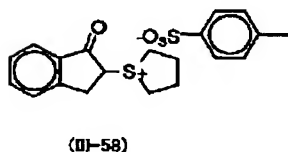
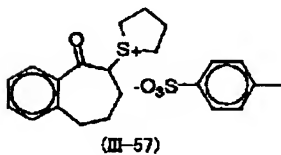
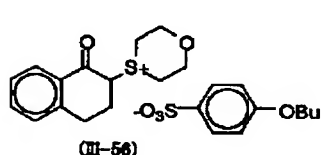
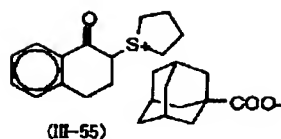
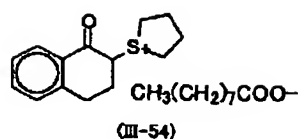
(III-52)



(III-53)

[0170]

[Formula 59]



[0171] (B) the addition of a component -- criteria [ total solids / of a positive-resist constituent ] -- carrying out -- general -- more than 1 mass % -- it is -- desirable -- 1.5 to 12 mass % -- it is two to 8 mass % still more preferably. (B) The compound which has the sulfonium salt or phenacyl sulfonium salt structure where it does not have a ring may be independently used for a component, and plurality may be mixed and used for it. Moreover, only a kind may use together other acid generating compounds which the following can use together, or more than one may be used together.

[0172] (B) In acid generating compound this invention which can be used together other than a component, other compounds which decompose by the exposure of an activity beam of light or a radiation, and generate an acid in addition to the (above-mentioned B) component may be used together. the amount of the acid generator used which can be used together with the component (B) of this invention -- a mole ratio (acid generator of (Component B)/and others) -- it is -- usually -- 100 / 0 - 20/80 -- desirable -- 100 / 0 - 40/60 -- it is 100 / 0 - 50/50 still more preferably. The well-known compounds which generate an acid by the exposure of the activity beam of light or radiation currently used for the photoinitiator of optical cationic

polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist as a photo-oxide generating agent in which such concomitant use is possible, and those mixture can be used choosing them suitably.

[0173] For example, the compound and disulfon compound which are represented by onium salt, such as diazonium salt, ammonium salt, phosphonium salt, iodonium salt, sulfonium salt, a selenonium salt, and arsonium salt, an organic halogenated compound, an organic metal / organic halogenide, the photo-oxide generating agent that has o-nitrobenzyl mold protective group, imino sulfonate, etc. and which photodissociate and generate a sulfonic acid can be mentioned.

[0174] Moreover, the compound of a publication can be used for the radical which generates an acid by the exposure of these activity beams of light or a radiation or the compound which introduced the compound into the principal chain or side chain of a polymer, for example, U.S. Pat. No. 3,849,137, Germany patent No. 3914407, JP,63-26653,A, JP,55-164824,A, JP,62-69263,A, JP,63-146038,A, JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc.

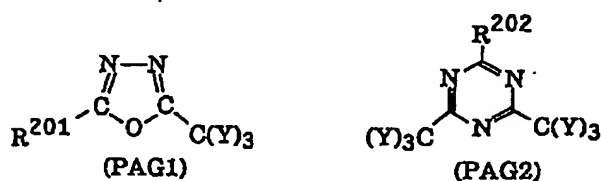
[0175] Furthermore, the compound which generates an acid by the light of a publication can also be used for U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0176] In the compound which decomposes by the exposure of the activity beam of light in which the above-mentioned concomitant use is possible, or a radiation, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0177]

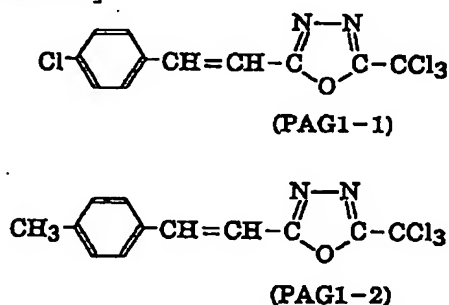
[Formula 60]



[0178] R201 shows among a formula the aryl group which is not permuted [ a permutation or ] and an alkenyl radical, and R202 shows the aryl group which is not permuted [ a permutation or ], an alkenyl radical, an alkyl group, and -C (Y)3. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

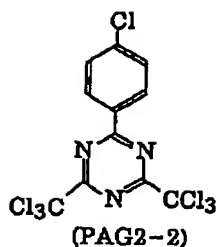
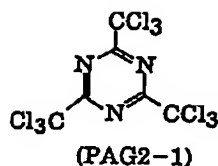
[0179]

[Formula 61]



[0180]

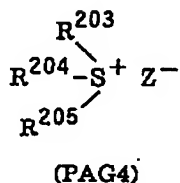
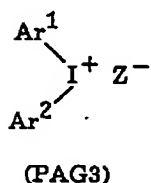
[Formula 62]



[0181] (2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0182]

[Formula 63]



[0183] Formulas Ar1 and Ar2 show respectively the aryl group which is not permuted [ a permutation or ] independently here. As a desirable substituent, an alkyl group, a halo alkyl group, a cycloalkyl radical, an aryl group, an alkoxy group, a nitro group, a carboxyl group, an alkoxy carbonyl group, a HIRODOKISHI radical, a sulfhydryl group, and a halogen atom are mentioned.

[0184] R203, R204, and R205 show respectively the alkyl group which is not permuted [ a permutation or ] and an aryl group independently. Preferably, they are the aryl group of carbon numbers 6–14, the alkyl groups of carbon numbers 1–8, and those permutation derivatives. As a desirable substituent, it is the alkoxy group of carbon numbers 1–8, the alkyl group of carbon numbers 1–8, a nitro group, a carboxyl group, a HIRODOKISHI radical, and a halogen atom to an aryl group, and they are the alkoxy group of carbon numbers 1–8, a carboxyl group, and an ARUKOSHIKI carbonyl group to an alkyl group.

[0185] Although Z<sup>-</sup> can show an opposite anion, for example, can mention condensation polykaryotic aromatic series sulfonic-acid anions, such as perfluoro alkane sulfonic-acid anions, such as BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, SiF<sub>6</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, a pentafluoro benzenesulfonic acid anion, and a naphthalene-1-sulfonic-acid anion, an anthraquinone sulfonic-acid anion, a sulfonic group content color, etc., it is not limited to these.

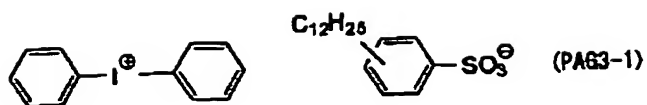
[0186] Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent.

[0187] Although the compound shown below as an example is mentioned, it is not limited to these.

[0188]

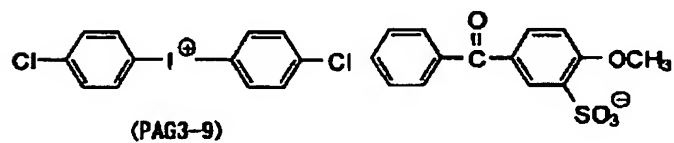
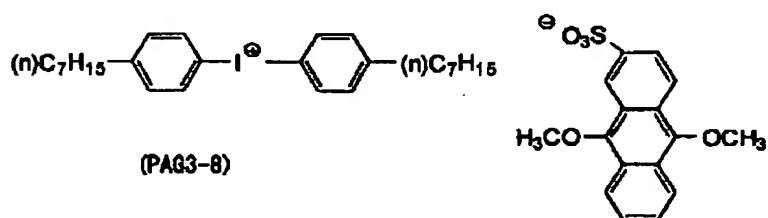
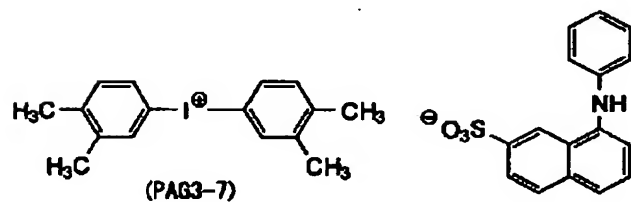
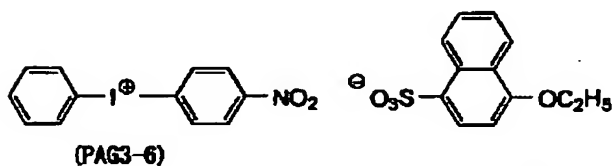
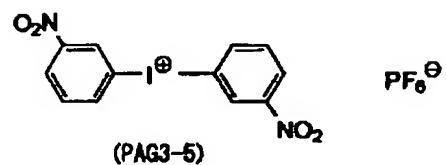
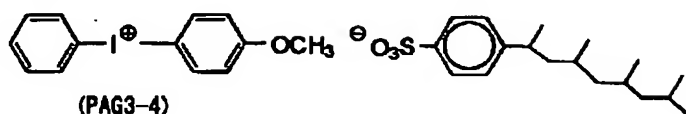
[Formula 64]





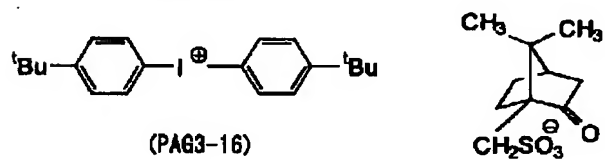
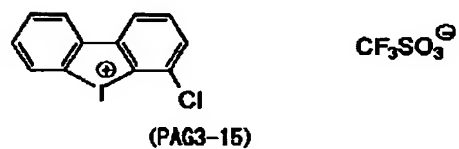
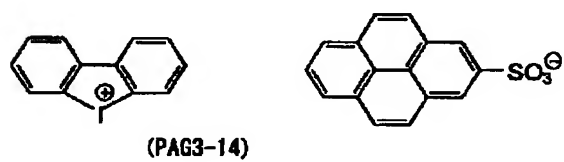
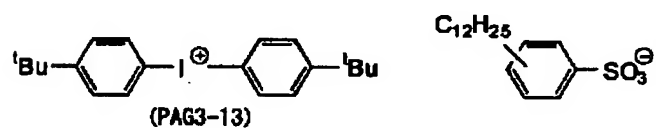
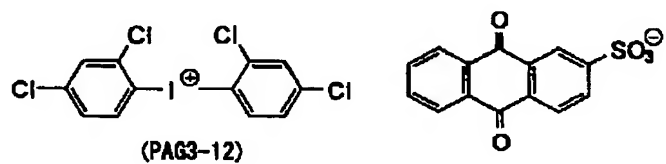
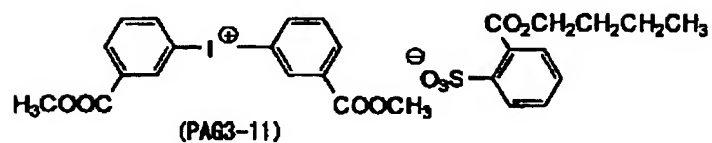
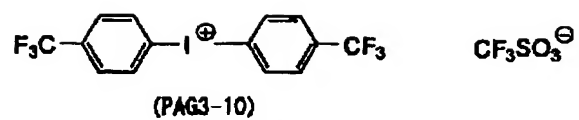
[0189]

[Formula 65]



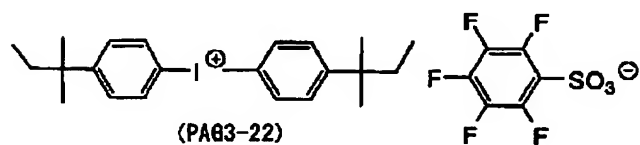
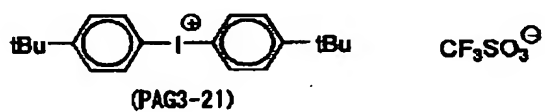
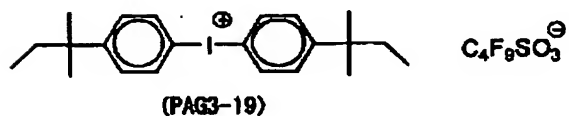
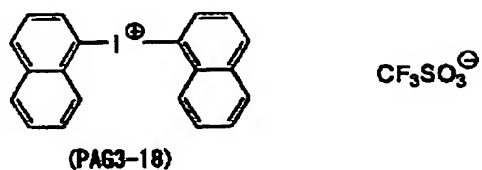
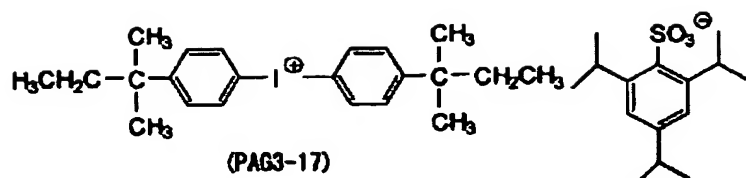
[0190]

[Formula 66]



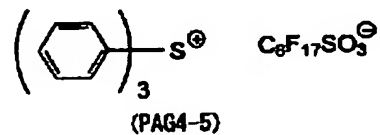
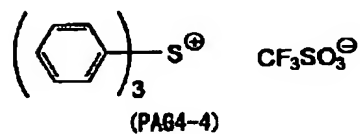
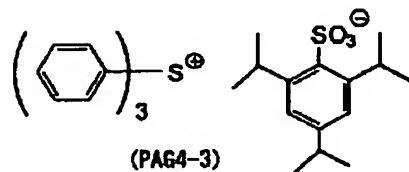
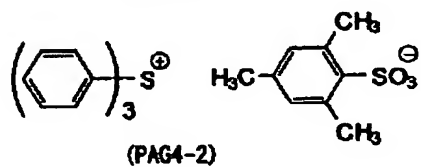
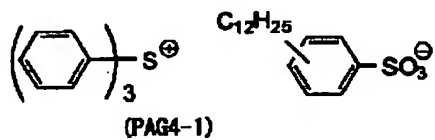
[0191]

[Formula 67]



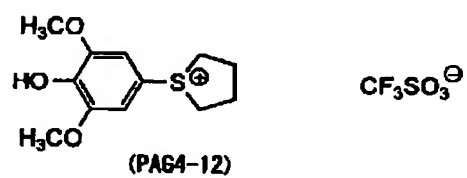
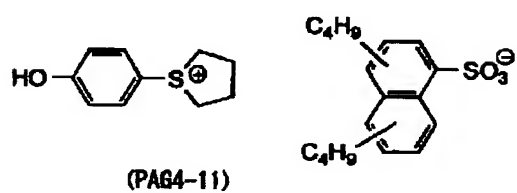
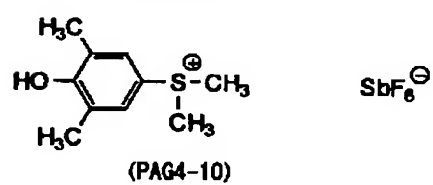
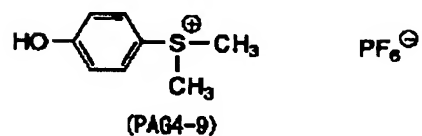
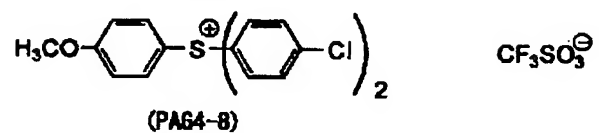
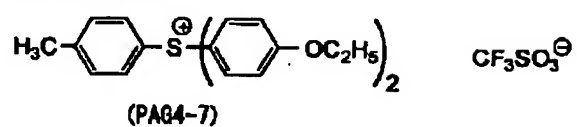
[0192]

[Formula 68]



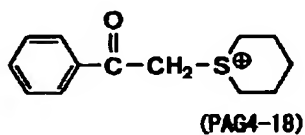
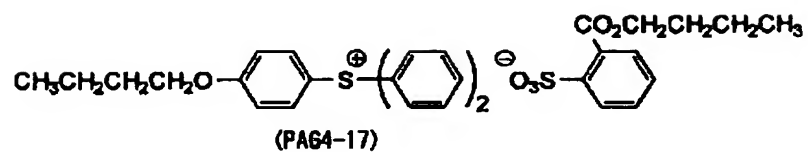
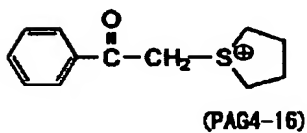
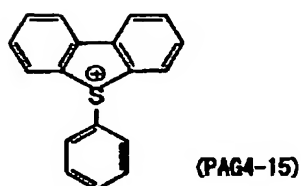
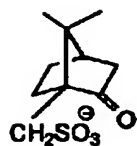
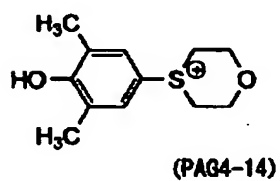
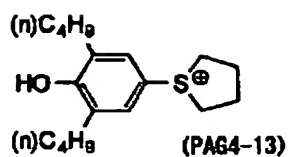
[0193]

[Formula 69]



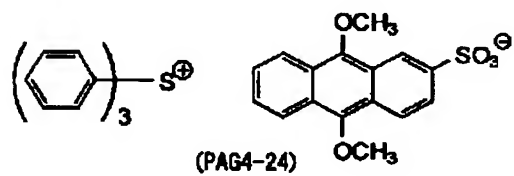
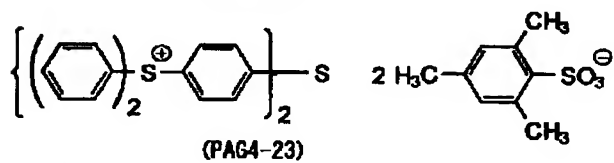
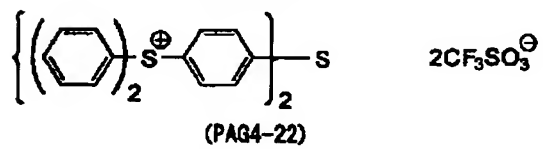
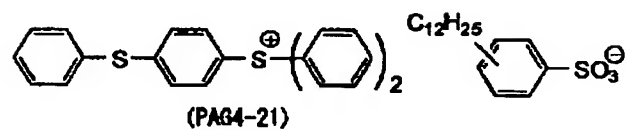
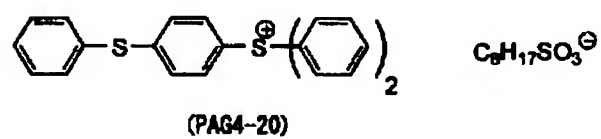
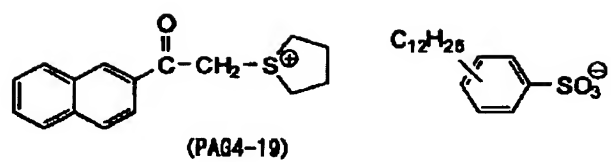
[0194]

[Formula 70]



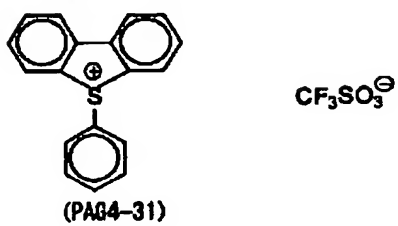
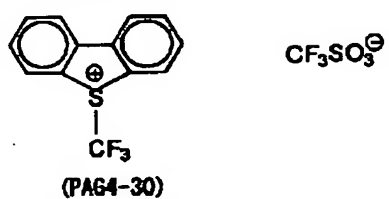
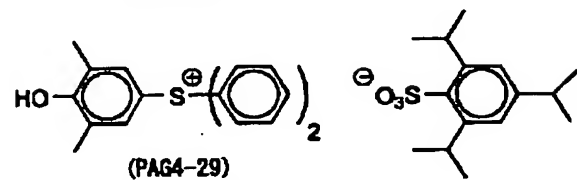
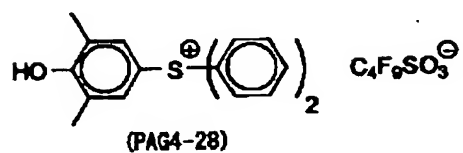
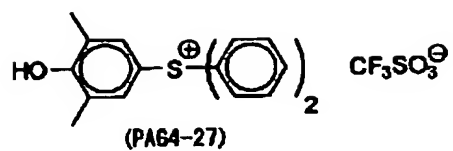
[0195]

[Formula 71]



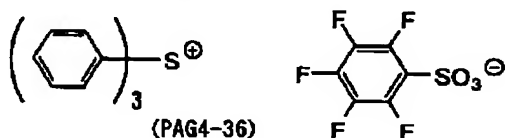
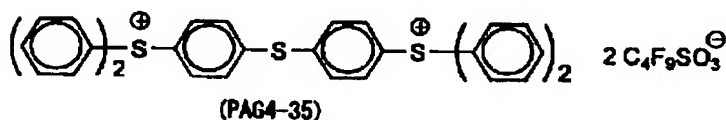
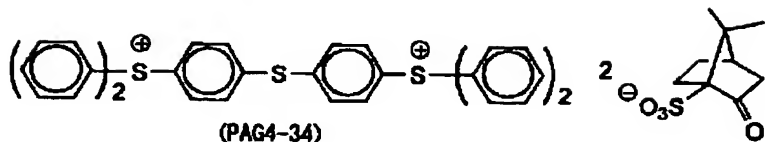
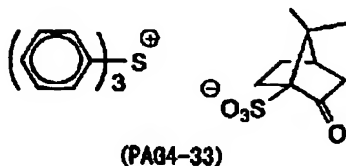
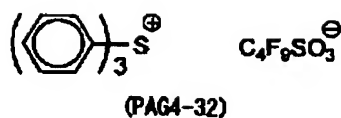
[0196]

[Formula 72]



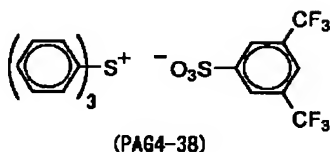
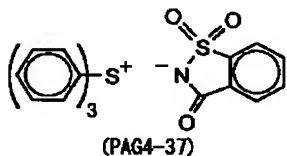
[0197]

[Formula 73]



[0198]

[Formula 74]

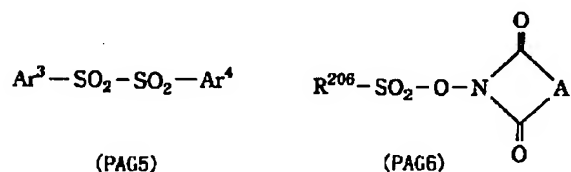


[0199] The above-mentioned onium salt shown by the general formula (PAG3) and (PAG4) is well-known, for example, can be compounded by the approach of a publication to U.S. Pat. No. 2,807,648 and said 4,247,473 numbers, JP,53-101,331,A, etc.

[0200] (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0201]

[Formula 75]

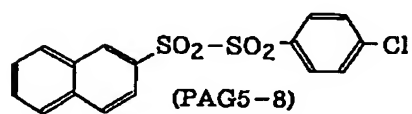
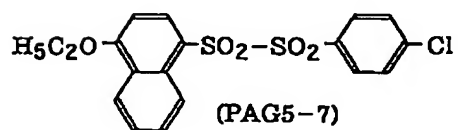
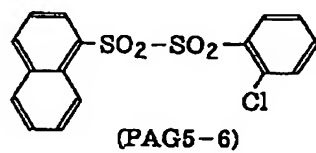
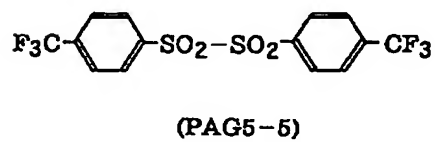
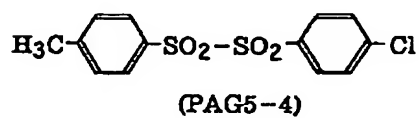
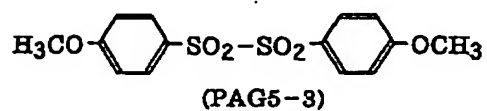
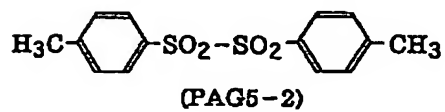
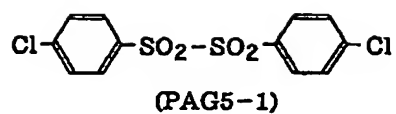


[0202] Ar3 and Ar4 show respectively the aryl group which is not permuted [ a permutation or ] independently among a formula. R206 shows the alkyl group which is not permuted [ a permutation or ] and an aryl group. A shows the alkylene group which is not permuted [ a permutation or ], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.



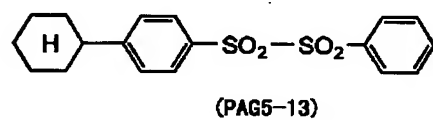
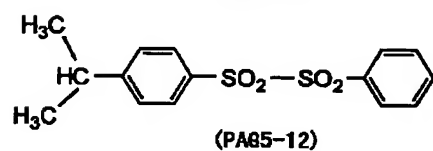
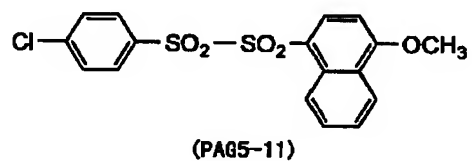
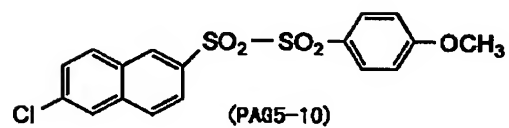
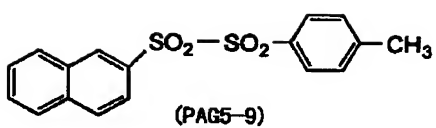
[0203]

[Formula 76]



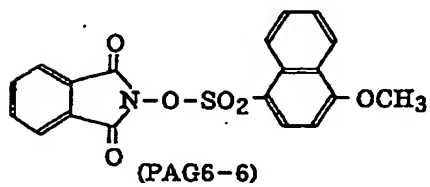
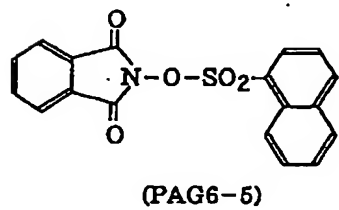
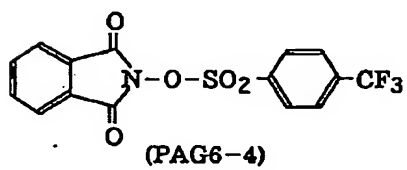
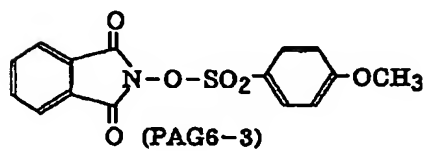
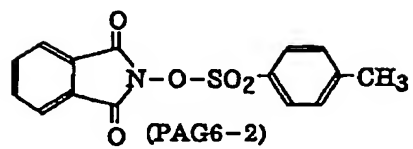
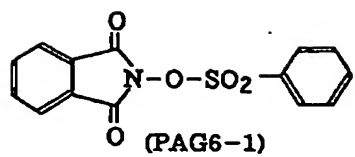
[0204]

[Formula 77]



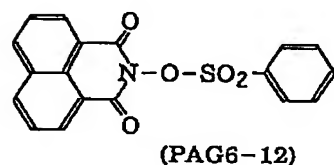
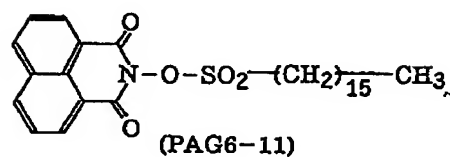
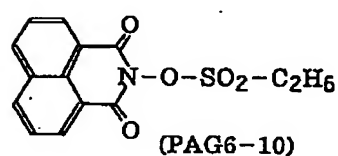
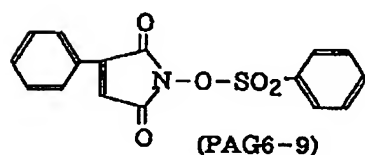
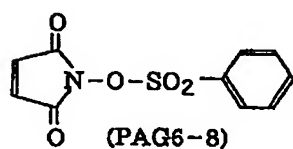
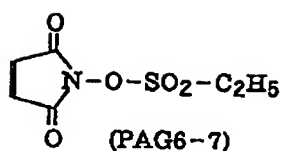
[0205]

[Formula 78]



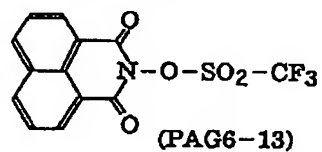
[0206]

[Formula 79]



[0207]

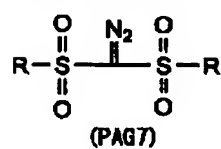
[Formula 80]



[0208] (4) The diazo disulfon derivative expressed with the following general formula (PAG7).

[0209]

[Formula 81]

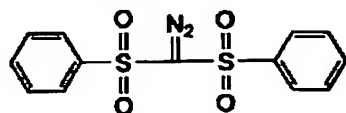


[0210] R expresses the shape of a straight chain, the letter of branching, an annular alkyl group,

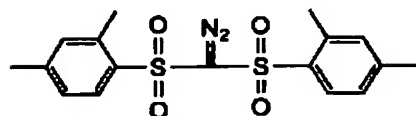
or the aryl group that may be permuted here. Although the compound shown below as an example is mentioned, it is not limited to these.

[0211]

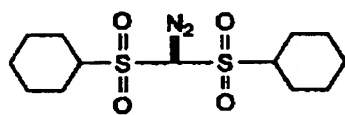
[Formula 82]



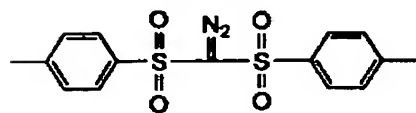
(PAG7-1)



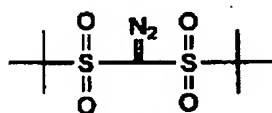
(PAG7-2)



(PAG7-3)



(PAG7-4)

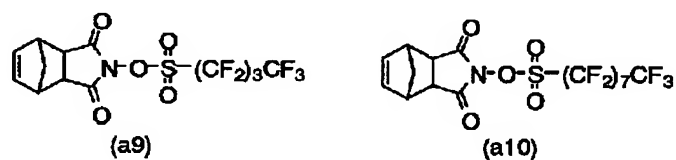
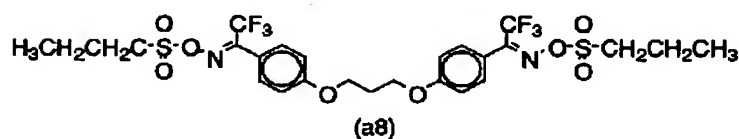
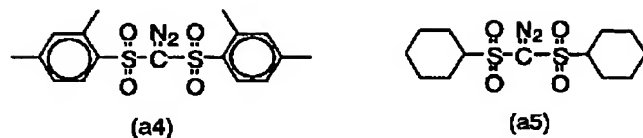
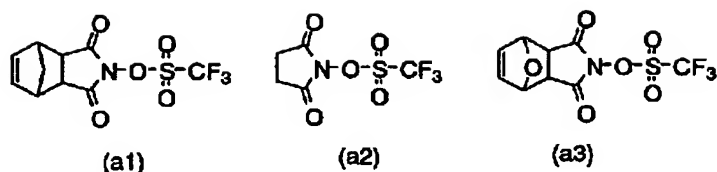


(PAG7-5)

[0212] In this invention, especially desirable concomitant use acid generators are an imino sulfonate derivative (PAG6) and a diazo sulfone derivative (PAG7) in the above, and especially the following can be mentioned.

[0213]

[Formula 83]



[0214] To the positive-resist constituent of [3] (C) fluorine system and/or silicon system surface-active-agent this invention, it is desirable to contain either a fluorine system and/or a silicon system surface active agent (a fluorochemical surfactant and a silicon system surface active agent, surface active agent containing both a fluorine atom and a silicon atom) and two sorts or more. By containing a fluorine system and/or a silicon system surfactant, especially, at the time of use of the exposure light source 220nm or less, the positive-resist constituents of this invention are 250nm or less, good sensibility, and resolution, and become possible [ giving a resist pattern with few adhesion and development defects ]. As a fluorine system and/or a silicon system surfactant, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, JP,2002-277862,A, a U.S. Pat. No. 5405720 specification, This No. 5360692 specification, this No. 5529881 specification, this No. 5296330 specification, This No. 5436098 specification, this No. 5576143 specification, \*\* A No. 5294511 specification and a surfactant given [ this ] in a No. 5824451 specification can be mentioned, and the surfactant of the following marketing can also be used as it is. As the fluorine system and/or silicon system surfactant of marketing which can be used For example, EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink & Chemicals, Inc. make), A fluorochemical surfactant or silicon system surfactants, such as Sir chlorofluocarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon

system surfactant.

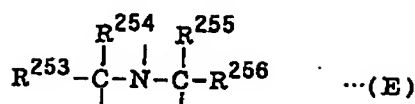
[0215] Moreover, the surfactant using the polymer which has the fluoro aliphatic series radical drawn from the fluoro aliphatic compound manufactured as a fluorine system and/or a silicon system surfactant by the telomerization method (called the telomer method) or the co-oligomerization method (called the oligomer method) other than a well-known thing as shown above can be used. A fluoro aliphatic compound is compoundable by the approach indicated by JP,2002-90991,A. As a polymer which has a fluoro aliphatic series radical, a copolymer with the monomer, acrylate (Pori (oxy-alkylene)), and/or (Pori (oxy-alkylene)) methacrylate which have a fluoro aliphatic series radical is desirable, and block copolymerization also of what is distributed irregularly may be carried out. Moreover, a unit which has the alkylene of chain length who the Pori (oxyethylene) radical, the Pori (oxypropylene) radical, the Pori (oxy-butylene) radical, etc. are mentioned, and is different as a Pori (oxy-alkylene) radical in the same chain length, such as Pori (block connection object of oxyethylene, oxypropylene, and oxyethylene) and the Pori (block connection object of oxyethylene and oxypropylene) radical, is sufficient. Furthermore, the copolymer not only a 2 yuan copolymer but more than the monomer which has two or more sorts of different fluoro aliphatic series radicals, and the 3 yuan system which copolymerized two or more sorts of different acrylate (Pori (oxy-alkylene)) (or methacrylate) etc. in coincidence is sufficient as the copolymer of the monomer and acrylate (Pori (oxy-alkylene)) (or methacrylate) which have a fluoro aliphatic series radical. For example, the megger fuck F178, F-470, F-473, F-475, F-476, and F-472 (Dainippon Ink & Chemicals, Inc. make) can be mentioned as a commercial fluorine system and/or a commercial silicon system surfactant. Furthermore, the copolymer of the acrylate (or methacrylate) and acrylate (Pori (oxy-alkylene)) (or methacrylate) which have C6F13 set, The copolymer of the acrylate (or methacrylate), acrylate (Pori (oxyethylene)) (or methacrylate), and acrylate (Pori (oxypropylene)) (or methacrylate) which have C6F13 set, The copolymer of the acrylate (or methacrylate) and acrylate (Pori (oxy-alkylene)) (or methacrylate) which have C8F17 set, The copolymer of the acrylate (or methacrylate), acrylate (Pori (oxyethylene)) (or methacrylate), and acrylate (Pori (oxypropylene)) (or methacrylate) which have C8F17 set etc. can be mentioned.

[0216] the amount of a fluorine system and/or the silicon system surface active agent used -- the positive-resist constituent whole quantity (except for a solvent) -- receiving -- desirable -- 0.0001 to 2 mass % -- it is 0.001 to 1 mass % more preferably.

[0217] To the constituent of [4] (D) acid diffusion inhibitor this invention, it is desirable after the exposure of an activity beam of light or a radiation to add an acid diffusion inhibitor in order to prevent the engine-performance fluctuation (T-top configuration formation of a pattern, sensibility fluctuation, pattern line-breadth fluctuation, etc.) by the passage of time to heat-treatment, the engine-performance fluctuation by the passage of time after spreading, and superfluous diffusion (degradation of resolution) of the acid at the time of heat-treatment after the exposure of an activity beam of light or a radiation further. As an acid diffusion inhibitor, it is an organic base nature compound, for example, is an organic base compound containing basic nitrogen, and four or more compounds are preferably used with the electric dissociation exponent value of a conjugate acid. Specifically, the structure of following type (A) - (E) can be mentioned.

[0218]

[Formula 84]



[0219] Here, it is R250 and R251. And R252 It may be the same, or you may differ and the permutation of a hydrogen atom, the alkyl group of 1-6 carbon numbers, the amino alkyl group of 1-6 carbon numbers, the hydroxyalkyl radical of 1-6 carbon numbers, or 6-20 carbon numbers or an unsubstituted aryl group is expressed, it may join together mutually and R251 and R252 may form a ring here. R253, R254, and R255 And R256 It may be the same, or you may differ and the alkyl group of 1-6 carbon numbers is expressed. Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [ a permutation or ] preferably.

[0220] As a desirable example, the aminopyridine which is not permuted [ the guanidine which is not permuted / a permutation or / a permutation, or ], The amino pyrrolidine which is not permuted [ the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or ], The imidazole which is not permuted [ the indazole which is not permuted / a permutation or /, a permutation or ], The pyrazine which is not permuted [ the pyrazole which is not permuted / a permutation or /, a permutation, or ], The imidazoline which is not permuted [ the pudding which is not permuted / the pyrimidine which is not permuted / a permutation or /, a permutation, or /, a permutation, or ], The amino alkyl morpholine which is not permuted [ the amino morpholine which is not permuted / the piperidine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or ] is mentioned.

Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0221] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, -tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, [0222] 3-amino pyrrolidine, a piperazine,



N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, a 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, A pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, Although 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, etc. are mentioned, it is not limited to this. These nitrogen-containing basicity compounds are independent, or are used together two or more sorts.

[0223] As for the operating rate in the constituent of an acid generator and an organic base nature compound, it is desirable that it is a (acid generator) / (organic base nature compound) (mole ratio) = 2.5-300. This mole ratio may serve as low sensibility less than by 2.5, resolving power may decline, and if 300 is exceeded, \*\*\*\* of a resist pattern may become large by the passage of time to exposure afterbaking processing, and resolving power may also decline. a (acid generator) -- / (organic base nature compound) (mole ratio) -- desirable -- 5.0-200 -- it is 7.0-150 still more preferably.

[0224] [5] Melt the constituent of component (1) solvent this invention of others which are used for the constituent of this invention to the solvent which dissolves each above-mentioned component, and apply it on a base material. As a solvent used here, ethylene dichloride, a cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, a methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monoethyl ether acetate, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, Propylene-glycol-monomethyl-ether acetate, toluene, ethyl acetate, Methyl lactate, ethyl lactate, methoxy methyl propionate, ethoxy ethyl propionate, methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N,N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. are desirable, and independent in these solvents -- or it is mixed and used.

[0225] In manufacture of a precision integrated circuit device etc., on substrates (example: transporence substrates, such as silicon / diacid-ized silicon leather \*\*, a glass substrate, and an ITO substrate etc.), the positive type photoresist constituent of this invention can be applied, it can irradiate by the ability using an activity beam of light or radiation drawing equipment next, and the pattern formation process to a resist film top can form a good resist pattern heating, development, a rinse, and by drying.

[0226] As an alkali developer of the positive-resist constituent of this invention A sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium silicate, Inorganic alkali, such as a meta-sodium silicate and aqueous ammonia, ethylamine, Secondary amines, such as primary amines, such as n propylamine, diethylamine, and G n butylamine Tertiary amines, such as triethylamine and methyl diethylamine, dimethylethanolamine, The water solution of alkali, such as annular amines, such as quaternary ammonium salt, such as alcoholic amines, such as a TORIETA no amine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and a choline, a pyrrole, and a piperidine, can be used. Furthermore, surfactants, such as alcohols, such as isopropyl alcohol, and the Nonion system, can also be used for the water solution of the above-mentioned alkali, carrying out suitable amount addition. the inside of these alkali developers -- desirable -- quaternary ammonium salt -- they are water solutions, such as tetramethylammonium hydroxide and a choline, still more preferably. the alkali concentration of an alkali developer -- usually -- 0.1 to 20 mass % -- desirable -- 0.2 to 15 mass % -- it is 0.5 to 10 mass % still more preferably. pH of an alkali developer -- usually -- 10.0-15.0 -- desirable -- 10.5-14.5 -- it is 11.0-14.0 still more preferably.

[0227]

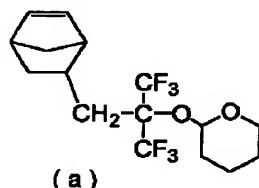
[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

[0228] 1 [ norbornene 9.4g (0.10 mols) and norbornene-2-carboxylic-acid t-butyl ester 19.4g (0.10 mols) ], 1, and a 2-trichlorofluoroethane 150ml solution were put in into the [synthetic example 1] 1L autoclave, and 200psi was pressurized under nitrogen-gas-atmosphere mind. Furthermore, tetra-FUROORO ethylene 20g (0.20 mols) was poured in, and it heated at 50 degrees C under stirring. It poured into it, having 2-trichlorofluoroethylene 15ml covered [ 1 / JI (4-t-butyl cyclohexyl) peroxy dicarbonate 1.2g / , 1, and ] them over this reaction mixture for 20 minutes, and stirring was continued for further 20 hours. It supplied after reaction termination, stirring reaction mixture violently in methanol 2L, and white resin was deposited. Resin (1)23.5g of this invention was obtained for depositing resin a \*\* exception and after desiccation under a vacuum. By GPC measurement, the molecular weight of resin (1) was 6,200 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (1), it was example (F-1) of structure / norbornene / (B-16) =45/30/25 in the mole ratio. In addition, the reference number of a structural unit points out the number given to the structural unit shown as an example by the resin (A) of above-mentioned this invention in this specification.

[0229] The [synthetic example 2] following monomer (a) 14.3g (0.04 mols), 3.9g [ of maleic anhydrides ] (0.04 mols), and t-butyl acrylate 2.6g (0.02 mols) was dissolved in MEK100ml, and it heated at 70 degrees C under the nitrogen air current. As a polymerization initiator, V-601 (product made from Wako Pure Chem Industry) 0.2g was added, and it stirred for 3 hours. Further V-601 [ 0.2g ] was added, and stirring was continued for 4 hours. Then, it supplied stirring reaction mixture violently in t-butyl methyl ether 1L, and white resin was deposited. Resin (2)12.1g of this invention was obtained for depositing resin a \*\* exception and after desiccation under a vacuum. By GPC measurement, the molecular weight of resin (2) was 8,900 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (2), it was example of structure (F-21) / maleic-anhydride / (B-4) =39/38/23 in the mole ratio.

[0230]

[Formula 85]

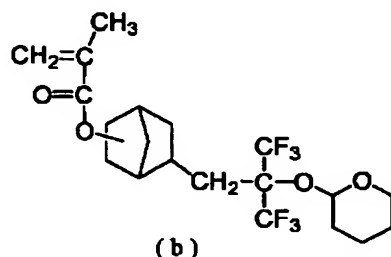


[0231] The [synthetic example 3] following monomer (b) 6.7g (0.015 mols), 2-methyl-2-adamantane methacrylate 1.4g (0.006 mols), Mevalonic-lactone-methacrylate 1.8g (0.009 mols) is dissolved in 1-methoxy-2-propanol 30ml. Under a nitrogen air current and churning, at 70 degrees C A polymerization initiator 2 and 2'-azobis (2,4-dimethylvaleronitrile) (product made from Wako Pure Chem Industry; trade name V-65) 0.1g, Monomer (b) 15.6g (0.035 mols), 2-methyl-2-adamantane methacrylate 3.3g (0.014 mols), The mevalonic-lactone-methacrylate 4.2g (0.021 mols) 1-methoxy-2-propanol 70ml solution was dropped over 2 hours. 0.1g of 2 hours after initiators was added, and the reaction was performed for further 2 hours. The temperature up was carried out to 90 degrees C after that, and

churning was continued for 1 hour. White resin was deposited after cooling reaction mixture radiationally by supplying agitating violently to ion exchange water / methanol (1/1) 1L. Resin (3) 15.8g of this invention was obtained after desiccation under reduced pressure of the obtained resin. When molecular weight was measured in GPC, it was 10,200 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (3), it was example (F-30)/(B-7)/(B-11) = of structure 48/21/31 in the mole ratio.

[0232]

[Formula 86]



[0233] The resin of this invention (A) similarly shown in Table 1 was compounded below the [synthetic examples 4-8].

[0234]

[Table 1]

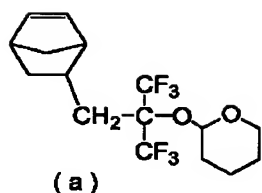
表1 本発明の樹脂(A)の合成

樹脂(A)	組成(樹脂中の構造単位とモル比)	分子量
(4)	(F-1)/(F-21)/(B-16) =48/33/19	4500
(5)	(F-50)/(B-7)/(B-11) =31/35/34	9200
(6)	(F-55)/無水マレイン酸/(B-4)=40/37/23	7400
(7)	(F-16)/無水マレイン酸/(B-8) =43/34/23	6300
(8)	(F-26)/無水マレイン酸/(B-12)=40/33/27	8900

[0235] 1 [ norbornene 9.4g (0.10 mols) and following (monomer a) 35.8g (0.10 mols) ], 1, and a 2-trichlorofluoroethylene 150ml solution were put in into the [synthetic example 9] 1L autoclave, and 200psi was pressurized under nitrogen-gas-atmosphere mind. Furthermore, tetra-FUROORO ethylene 20g (0.20 mols) was poured in, and it heated at 50 degrees C under stirring. It poured into it, having 2-trichlorofluoroethane 15ml covered [ 1 / JI (4-t-butyl cyclohexyl) peroxy dicarbonate 1.2g / , 1, and ] them over this reaction mixture for 20 minutes, and stirring was continued for further 20 hours. It supplied after reaction termination, stirring reaction mixture violently in methanol 2L, and white resin was deposited. Resin (9) 37.4g of this invention was obtained for depositing resin a \*\* exception and after desiccation under a vacuum. By GPC measurement, the molecular weight of resin (13) was 8,800 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (9), it was example (F-1)/of structure (F-21) / norbornene =48/30/22 in the mole ratio.

[0236]

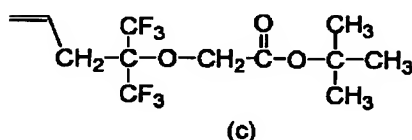
[Formula 87]



[0237] Instead of the monomer (a) of the example 9 of the [synthetic example 10] composition, following (monomer c) 32.2g (0.04 mols) was used, and resin (10) 34.1g of this invention was compounded like the synthetic example 9 below. By GPC measurement, the molecular weight of resin (10) was 7,400 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (10), it was example (F-1)/of structure (F-15) / norbornene =49/25/26 in the mole ratio.

[0238]

[Formula 88]



[0239] The resin of this invention (A) similarly shown in Table 2 was compounded below the [synthetic examples 11-14].

[0240]

[Table 2]

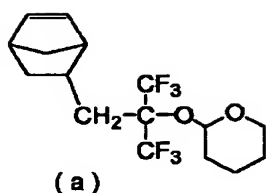
表2 本発明の樹脂(A)の合成

樹脂(A)	組成(樹脂中の構造単位とモル比)	分子量
(11)	(F-1)/(F-20)/(B-4) =48/30/22	9300
(12)	(F-2)/(F-22)/(B-4) =42/38/19	7900
(13)	(F-12)/(F-21)/ノルボルネン =23/38/39	5800
(14)	(F-1)/(F-16)/(B-16) =34/26/40	9500

[0241] The [synthetic example 15] following monomer (a) 14.3g (0.04 mols), 3.9g [ of maleic anhydrides ] (0.04 mols), and norbornene-2-carboxylic-acid 2-(perfluoro octyl) ethyl 11.7g (0.02 mols) was dissolved in MEK100ml, and it heated at 70 degrees C under the nitrogen air current. As a polymerization initiator, V-601 (product made from Wako Pure Chem Industry) 0.2g was added, and it stirred for 3 hours. Further V-601 [ 0.2g ] was added, and stirring was continued for 4 hours. Then, it supplied stirring reaction mixture violently in t-butyl methyl ether 1L, and white resin was deposited. Resin (15) 16.2g of this invention was obtained for depositing resin a \*\* exception and after desiccation under a vacuum. By GPC measurement, the molecular weight of resin (15) was 8,700 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (15), it was example (F-21)/of structure (F-55) / maleic-anhydride =42/18/40 in the mole ratio.

[0242]

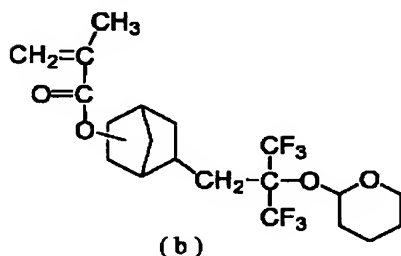
[Formula 89]



[0243] The [synthetic example 16] following monomer (b) 6.7g (0.015 mols), 2-(perfluoro octyl) ethyl methacrylate 2.7g (0.005 mols), 2-methyl-2-adamantane methacrylate 1.2g (0.005 mols), Mevalonic-lactone-methacrylate 1.0g (0.005 mols) is dissolved in 1-methoxy-2-propanol 30ml. Under a nitrogen air current and churning, at 70 degrees C A polymerization initiator 2 and 2'-azobis (2,4-dimethylvaleronitrile) (product made from Wako Pure Chem Industry; trade name V-65) 0.1g, Monomer (b) 15.6g (0.035 mols), 2-(perfluoro octyl) ethyl methacrylate 6.4g (0.012 mols), The 1-methoxy-2-propanol 70ml solution (2-methyl-2-adamantane methacrylate 2.8g (0.012 mols) and mevalonic-lactone-methacrylate 2.4g (0.012 mols)) was dropped over 2 hours. 0.1g of 2 hours after initiators was added, and the reaction was performed for further 2 hours. The temperature up was carried out to 90 degrees C after that, and churning was continued for 1 hour. White resin was deposited after cooling reaction mixture radiationally by supplying agitating violently to ion exchange water / methanol (1/1) 1L. Resin (16) 21.5g of this invention was obtained after desiccation under reduced pressure of the obtained resin. When molecular weight was measured in GPC, it was 10,500 in the weighted mean (Mw). Moreover, when C13-NMR measurement investigated the presentation of resin (16), it was example (F-30)/(F-48)/(B-7)/(B-11) = of structure 48/15/18/19 in the mole ratio.

[0244]

[Formula 90]



[0245] The resin (A) of this invention similarly shown in Table 3 was compounded below the [synthetic examples 17-19].

[0246]

[Table 3]

表3 本発明の樹脂(A)の合成

樹脂(A)	組成(樹脂中の構造単位とモル比)	分子量
(17)	(F-15)/(F-58)/無水マレイン酸=30/24/46	9700
(18)	(F-25)/(F-55)/(B-4)/無水マレイン酸=21/18/25/36	7800
(19)	(F-30)/(F-54)/(B-7)/(B-13)=38/15/31/16	9900

[0247] [Synthetic example 20] 4-[bis(trifluoromethyl)-hydroxymethyl] styrene 13.5g (0.05 mols) and methacrylonitrile 3.4g (0.05 mols) were dissolved in 100ml of N,N-dimethylacetamide, and it heated at 70 degrees C under the nitrogen air current. 2 and 2'-azobis

(2,4-dimethylvaleronitrile) (product made from Wako Pure Chem Industry; trade name V-65) 0.1g was added as a polymerization initiator, and it stirred for 3 hours. Further V-65 [ 0.1g ] was added, and stirring was continued for 4 hours. Then, it supplied stirring reaction mixture violently in a methanol / t-butyl methyl ether (1/1) 1L, and white resin was deposited. Depositing resin was dissolved in THF100ml a \*\* exception and after desiccation under a vacuum, ethyl-vinyl-ether 2.9g (0.04 mols) was added, the amount addition of catalysts of the p-toluenesulfonic acid was carried out, and it stirred at the room temperature for 8 hours. Triethylamine was supplied to reaction mixture, having made it stop and stirring violently the amount of 2 double, in addition reaction of a p-toluenesulfonic-acid catalyst in ultrapure water 3L. Depositing resin was dried the \*\* exception and resin (20) 14.1g of this invention was obtained. By GPC measurement, the molecular weight of resin (20) was 10,900 in the weighted mean (Mw). Moreover, when C13-NMR and IR measurement investigated the presentation of resin (20), it was example (F-39)/(F-42)/(C-10) =of structure16/36/48 in the mole ratio. [0248] The resin (A) of this invention shown in Table 4 was compounded like below the [synthetic examples 21-23].

[0249]

[Table 4]

表4 本発明の樹脂(A)の合成

樹脂(A)	組成(樹脂中の構造単位とモル比)	分子量
(21)	(F-39)/(F-41)/(C-10) =14/38/48	11100
(22)	(F-39)/(F-43)/(C-10) =13/39/48	12600
(23)	(F-1)/(B-4)/(C-8) =43/34/23	7400

[0250] [The synthetic examples 24-41]

the tetrahydrofuran after the each mole ratios' 50/'s50 coming out comparatively and teaching 4-(2-hydroxy hexafluoro isopropyl) styrene (Central Glass Co., Ltd. make) and 4-(1-methoxyethoxy) styrene (TOSOH CORP. make) into 100ml 3 opening flask equipped with synthetic reflux tubing and nitrogen installation tubing of resin (25) -- adding -- reaction mixture of 30 % of the weight of monomer concentration -- all -- 30g was adjusted. It was heated to 65 degrees C under stirring and a nitrogen air current. a polymerization initiator 2 and 2'-azobis (2,4-dimethylvaleronitrile) (the product made from Wako Pure Chem Industry; trade name V-65) -- the mol of said two monomer sum totals -- a number -- receiving -- 5.0-mol % -- it adds, and it was made to react for 8 hours, stirring under a nitrogen air current The polymer which added hexane 200ml and was generated was settled from the solution to the obtained reaction mixture, and separation purification of the unreacted monomer was carried out. The polymer presentation searched for from C13NMR was 49/51. When the obtained polymer was analyzed in GPC (standard polystyrene conversion among a THF solvent), weight average molecular weight 10,200, degree of dispersion 2.20, and a with a molecular weight of 1000 or less contained in a polymer rate were 15 % of the weight. Hereafter, the resin (A) of this invention similarly shown in Table 5 was compounded.

[0251]

[Table 5]

表5 本発明の樹脂(A)の合成

樹脂(A)	組成(樹脂中の構造単位とモル比)	分子量
(24)	(I I-1)/(A-1)=48/52	8900
(25)	(I I-1)/(A-2)=49/51	10200
(26)	(I I-1)/(A-3')=53/47	5800
(27)	(I I-1)/(A-10)=61/39	9200
(28)	(I I-1)/(A-19)=64/36	8500
(29)	(I I-1)/(A-34)=60/40	8600
(30)	(I I-1)/(A-35)=51/49	8800
(31)	(I I-2)/(A-19)=64/36	10100
(32)	(I I-4)/(A-26)=52/48	12100
(33)	(I I-1)/(B-7)=78/22	9200
(34)	(I I-1)/(A-19)/(V I I-2) =64/26/10	9200
(35)	(I I-1)/(A-19)/(F-7) =58/33/9	9500
(36)	(I I-1)/(B-4)/(V I I-2) =61/24/15	10600
(37)	(I I-3)/(B-8)/(F-7) =49/36/15	9200
(38)	(I I-4)/(B-12')/(F-24) =59/33/8	8300
(39)	(II-1)/(A-1)/(B-6) =48/30/22	9200
(40)	(II-1)/(A-2)/(B-8) =51/39/10	8400
(41)	(II-1)/(A-1)/(B-1)/(C-1) =48/36/11/5	10200

[0252] The sample solution which dissolved 1.2g of resin of the (A) component shown in examples 1-26, the example 1 of a comparison - the 3 above-mentioned tables 1-5, 0.03g (the (B) component and other acid generators of this invention) of photo-oxide generating agents, 100 ppm of surfactants of the (C) component, and 0.0012g of basic compounds of the (D) component in 19.6g of solvents was filtered with the 0.1-micrometer polytetrafluoroethylene filter, and the positive-resist constituent was prepared (Table 6). In addition, in Table 6, the reference number of a photo-oxide generating agent points out the number given to the example indicated to the above in a specification.

[0253]

[Table 6]

表6

実施例	(A)樹脂	光酸発生剤 (重量比)	(C)界面活性剤	(D)塩基性化合物 (重量比)	溶剤 (重量比)
1	(1)	(II-1)	W-1	(N-3)	S-2
2	(2)	(II-2)	W-1	(N-1)	S-2
3	(3)	(II-3)	W-1	(N-1)/(N-2)= 50/50	S-2
4	(4)	(II-4)	W-1	(N-4)	S-2
5	(5)	(II-5)	W-1	(N-2)	S-2
6	(6)	(II-6)	W-1	(N-6)	S-2
7	(7)	(II-7)	W-2	(N-3)	S-2
8	(8)	(II-8)	W-1	(N-7)	S-2
9	(9)	(II-9)	W-1	(N-5)	S-2/S-3= (80/20)
10	(10)	(II-10)	W-1	(N-4)	S-2
11	(11)	(II-11)	W-2	(N-2)/(N-3)= 50/50	S-2/S-3= (90/10)
12	(12)	(II-12)	W-1	(N-5)	S-2
13	(13)	(II-13)	W-1	(N-3)	S-2
14	(14)	(II-14)	W-1	(N-1)	S-2
15	(15)	(II-15)	W-1	(N-2)	S-2/S-3= (70/30)
16	(17)	(II-16)	W-2	(N-6)	S-2
17	(18)	(II-17)	W-2	(N-1)	S-2
18	(19)	(II-19)	W-1	(N-7)	S-2
19	(21)	(II-20)	W-1	(N-7)	S-2
20	(22)	(II-21)	W-1	(N-1)	S-2
21	(23)	(II-22)	W-1	(N-1)	S-2
22	(39)	(II-11)/(III-48)= 50/50	W-2	(N-2)	S-2
23	(41)	(II-11)/(III-1)= 50/50	W-1	(N-3)	S-1/S-2= (5/95)
24	(24)	(II-11)/(PAG4-1)= 50/50	W-1	(N-3)	S-2/S-3= (90/10)
25	(26)	(II-11)/(PAG5-1)= 50/50	W-1	(N-4)	S-1/S-2= (5/95)
26	(32)	(II-11)/(PAG7-1)= 50/50	W-1	(N-5)	S-2
比較例1	(1)	(PAG4-1)	W-1	(N-2)	S-2
比較例2	(26)	(PAG4-1)	W-1	(N-3)	S-1/S-2= (5/95)
比較例3	(p-1-(エトキシ)エトキシ)スチレン/p-ヒドロキシスチレン=35/65	(II-1)	W-2	(N-2)	S-2

[0254] In addition, the cable address of a surfactant means the following among the above-mentioned table.

W-1: Megger fuck F176 (Dainippon Ink make) (fluorine system)

W-2: Megger fuck R08 (Dainippon Ink make) (a fluorine and silicon system)

[0255] The cable address of a basic compound means the following among the above-mentioned table.

N-1: 1 and 5-diazabicyclo [4.3.0]-5-nonene N-2: -- 2, 4, and 5-triphenyl imidazole

N-3: N-hydroxyethyl piperidine N- 4, 2, the 6-diisopropyl aniline N-5: dicyclohexyl monomethylamine N-6: hexamethylenetetramine N-7: 1, and 8-diazabicyclo [5.4.0]-7-undecene

[0256] Furthermore, the cable address of a solvent means the following.

S-1: Ethyl lactate S-2: propylene-glycol-monomethyl-ether acetate S-3 : propylene glycol monomethyl ether [0257] It evaluated as follows about the transmission of the positive-resist

constituent obtained above, DOF (defocusing latitude), and negative-ization. An evaluation result is shown in Table 7.



(1) transmissometry -- spin coating of the positive-resist constituent of these was carried out at MgF2 substrate, it carried out \*\*--KU during 90 seconds at 100 degrees C using the hot plate, and the resist layer with a thickness of 200nm was created on the MgF2 substrate. The permeability in 157nm was measured using the vacuum-ultraviolet photometer (the Jasco make, VUV200S).

[0258] (2) The antireflection film (ARC25: BURYUWA Saiensu-Sha make) was applied to 600A homogeneity on the silicon substrate by the DOF (defocusing latitude) evaluation spin coater, and stoving was performed for 190 degrees C and 240 seconds. Then, each positive-resist constituent was applied by the spin coater, for 120 degrees C and 90 seconds, stoving was performed and the resist film with a thickness of 0.3 micrometers was obtained. After performing image formation using a CanonKrF excimer stepper (FPA-3000EX5:NA0.60) and carrying out afterbaking in 110 degrees C and 90 seconds to the obtained resist film, the 0.20-micrometer last shipment pattern was made to form by carrying out present Quercus acutissima in a 0.262-N TMAH water solution. The defocusing latitude (DOF) of 0.20 micrometers was observed in the light exposure reproducing 0.20-micrometer Rhine and a tooth space (= 1/1).

[0259] (3) It applied on the silicon wafer which performed hexamethylenedisilazane processing for negative-ized evaluation each positive-resist constituent by the spin coater, stoving was carried out on the hot plate for 90 seconds at 120 degrees C, and the resist film of 0.1 micrometers of thickness was obtained. The light exposure of the range of 1 mJ/cm<sup>2</sup> - 100 mJ/cm<sup>2</sup> was irradiated to the obtained resist film using laser radiation equipment VUVES-4500 [ 157nm ] (Litho Tech Japan make). It heated with the hot plate for [ 110 degrees-C ] 90 seconds after exposure, and the 0.262-N TMAH water solution performed the development. Thickness was measured after development, and in the high light exposure field of 50 mJ/cm<sup>2</sup> - 100 mJ/cm<sup>2</sup>, what O and a residual membrane are regarded as in what the resist film is dissolving completely was made into x noting that there was concern of negative-izing.

[0260]

[Table 7]

表7

実施例	透過率 @157 $\mu$ m[%]	DOF[ $\mu$ m]	ネガ化
1	48	0.7	○
2	43	0.7	○
3	45	0.7	○
4	42	0.8	○
5	48	0.7	○
6	49	0.7	○
7	46	0.8	○
8	45	0.6	○
9	44	0.7	○
10	42	0.8	○
11	47	0.7	○
12	48	0.9	○
13	49	0.8	○
14	46	0.8	○
15	45	0.7	○
16	44	0.7	○
17	42	0.7	○
18	47	0.8	○
19	43	0.7	○
20	45	0.8	○
21	42	0.8	○
22	48	0.7	○
23	49	0.7	○
24	46	0.8	○
25	45	0.7	○
26	44	0.7	○
比較例1	34	0.4	×
比較例2	35	0.5	×
比較例3	18	0.6	○

[0261] The result of Table 7 shows the constituent of this invention having high transmission, and defocusing latitude being large, and the resist film dissolving completely substantially also in evaluation of negative-izing, and excelling.

[0262] The antireflection film (ARC25, BURYUWA Saiensu-Sha make) was applied to 600A homogeneity on the silicon substrate by the spin coater, and desiccation was performed for 190 degrees C and 240 seconds. Then, after applying each positive-resist constituent by the spin coater, for 120 degrees C and 90 seconds, desiccation was performed and the resist film with a thickness of 0.12 micrometers was obtained. The light exposure of the range of 1 – 100 mJ/cm<sup>2</sup> was irradiated through the mask for adhesion mold exposure to the obtained resist film using laser radiation equipment VUVES-4500 [ 157nm ] (Litho Tech Japan Corp. make). The 0.35-micrometer last shipment pattern was made to form by heating with a hot plate for 110 degrees C and 90 seconds after exposure, and performing a development in a 0.262-N TMAH water solution. In the light exposure reproducing 0.35-micrometer Rhine and a tooth space (1/1), LER (the Rhine edge roughness) and a skirt length configuration were observed as follows. The result is shown in the following table 8. In addition, in front Naka, resolution is 0.35 micrometers or more and that it is with “-” means that the evaluation concerned was not able to be carried out.

[0263] (4) Evaluation of the LER (Rhine edge roughness) evaluation LER (the Rhine edge roughness) used the length measurement scanning electron microscope (CD-SEM), and measured it about the edge of a 0.35-micrometer Rhine and a tooth space (1/1). Within the measurement monitor, the pattern edge was detected in two or more locations, and distribution (3sigma) of the variation in the detection location was made into the index of edge roughness. A value is so desirable that it is small.

[0264] (5) Skirt length configuration evaluation dimension size 0.35micrometer Rhine and a

tooth-space pattern were observed by SEM (Hitachi Make S-8840), and the following type estimated extent of the skirt length configuration shown in drawing 1. It is shown that extent of skirt length is so small that a numeric value is small.

A formula  $(B-A) / 2B \times 100 (\%)$

[0265]

[Table 8]

表8

	LER	裾引き形状
実施例 1	4.9	15
実施例 2	5.0	14
実施例 3	5.1	13
実施例 4	5.1	14
実施例 5	4.9	12
実施例 6	5.0	15
実施例 7	4.9	12
実施例 8	4.8	13
実施例 9	5.1	14
実施例 10	5.0	15
実施例 11	4.9	13
実施例 12	4.8	12
実施例 13	4.9	14
実施例 14	4.7	13
実施例 15	4.8	15
実施例 16	4.9	13
実施例 17	4.8	14
実施例 18	4.8	15
実施例 19	4.9	15
実施例 20	5.1	16
実施例 21	4.9	15
実施例 22	5.0	14
実施例 23	5.2	13
実施例 24	6.1	13
実施例 25	5.9	13
実施例 26	5.0	15
比較例 1	9.3	30
比較例 2	10.8	35
比較例 3	—	—

[0266] It is clear from Table 8 that the positive-resist constituent's of this invention the Rhine edge roughness is small and skirt length is small.

[0267] The sample solution which dissolved 1.2g of resin of the (A) component shown in examples 27-69, the example 4 of a comparison - the 6 above-mentioned tables 1-5, 0.03g (the (B) component and other acid generators of this invention) of photo-oxide generating agents, 100 ppm of surfactants of the (C) component, and 0.0012g of basic compounds of the (D) component in 19.6g of solvents was filtered with the 0.1-micrometer polytetrafluoroethylene filter, and the positive-resist constituent be prepared (Tables 9 and 10). In addition, in Tables 9 and 10, the reference number of a photo-oxide generating agent points out the number given to the example indicated to the above in a specification.

[0268]

[Table 9]

表9

実施例	(A)樹脂	(B)光酸発生剤 (重量比)	(C)界面活性剤	(D)塩基性 化合物 (重量比)	溶剤 (重量比)
27	(1)	(III-1)	W-1	(N-3)	S-2
28	(2)	(III-2)	W-1	(N-1)	S-2
29	(3)	(III-5)	W-1	(N-1)/(N-2)= 50/50	S-2
30	(4)	(III-6)	W-1	(N-4)	S-2
31	(5)	(III-7)	W-1	(N-2)	S-2
32	(6)	(III-8)	W-1	(N-6)	S-2
33	(7)	(III-9)	W-2	(N-3)	S-2
34	(8)	(III-10)	W-1	(N-7)	S-2
35	(9)	(III-11)	W-1	(N-5)	S-2/S-3= (80/20)
36	(10)	(III-12)	W-1	(N-4)	S-2
37	(11)	(III-13)	W-2	(N-2)/(N-3)= 50/50	S-2/S-3= (90/10)
38	(12)	(III-14)	W-1	(N-5)	S-2
39	(13)	(III-15)	W-1	(N-3)	S-2
40	(14)	(III-16)	W-1	(N-1)	S-2
41	(15)	(III-17)	W-1	(N-2)	S-2/S-3= (70/30)
42	(17)	(III-18)	W-2	(N-6)	S-2
43	(18)	(III-23)	W-2	(N-1)	S-2
44	(19)	(III-25)	W-1	(N-7)	S-2
45	(21)	(III-28)	W-1	(N-7)	S-2
46	(22)	(III-31)	W-1	(N-1)	S-2
47	(23)	(III-36)	W-1	(N-1)	S-2
48	(24)	(III-42)	W-2	(N-2)	S-2
49	(26)	(III-44)	W-1	(N-3)	S-1/S-2= (5/95)
50	(28)	(III-46)	W-1	(N-3)	S-2/S-3= (90/10)
51	(31)	(III-47)	W-1	(N-4)	S-1/S-2= (5/95)
52	(32)	(III-1)/(III-48)= 50/50	W-1	(N-5)	S-2
53	(33)	(III-49)	W-1	(N-2)	S-2
54	(34)	(III-1)/(III-50)= 50/50	W-1	(N-3)	S-2
55	(35)	(III-53)	W-2	(N-1)	S-2
56	(36)	(III-1)/(III-54)= 50/50	W-1	(N-6)	S-2/S-4= (95/5)

[0269]

[Table 10]

表10

実施例	(A)樹脂	(B)光酸発生剤 (重量比)	(C)界面活性剤	(D)塩基性化合物 (重量比)	溶剤 (重量比)
57	(37)	(Ⅲ-1)/(Ⅲ-55)= 50/50	W-1	(N-4)	S-1/S-2= (10/90)
58	(38)	(Ⅲ-59)	W-1	(N-7)	S-2
59	(39)	(Ⅲ-60)	W-1	(N-5)	S-2
60	(40)	(Ⅲ-61)	W-2	(N-6)	S-2/S-5= (85/5)
61	(41)	(Ⅲ-62)	W-1	(N-2)	S-2
62	(24)	(Ⅲ-1)/(Ⅲ-63)= 50/50	W-1	(N-4)	S-1/S-2= (40/60)
63	(25)	(Ⅲ-1)/(Ⅲ-64)= 50/50	W-1	(N-5)	S-2/S-3= (50/50)
64	(26)	(Ⅲ-1)/(PAG4- 1)= 50/50	W-4	(N-6)	S-2
65	(27)	(Ⅲ-1)/(PAG4- 2)= 50/50	W-1	(N-5)	S-2
66	(28)	(Ⅲ-1)/(Ⅲ-5)= 50/50	W-1	(N-7)	S-2/S-6= (95/5)
67	(29)	(Ⅲ-1)/(PAG7- 1)= 50/50	W-3	(N-2)	S-2/S-3= (50/50)
68	(30)	(Ⅲ-1)/(PAG5- 2)= 50/50	W-1	(N-3)	S-2/S-7= (95/5)
69	(26)	(Ⅲ-1)/(PAG5- 2)= 50/50	W-1	(N-4)	S-2
比較例4	(1)	(PAG4-1)	W-1	(N-2)	S-2
比較例5	(26)	(PAG4-1)	W-2	(N-3)	S-1/S-2= (5/95)
比較例6	(p-1-(エトキシ)エトキシ)スチレン/p-ヒドロキシスチレン (36/64)	(Ⅲ-1)	W-1	(N-2)	S-2

[0270] In addition, the cable address of a surfactant means the following among the above-mentioned table.

W-1: Megger fuck F176 (Dainippon Ink make) (fluorine system)

W-2: Megger fuck R08 (Dainippon Ink make) (a fluorine and silicon system)

W-3: polysiloxane polymer KP-341 (silicon system) (Shin-Etsu Chemical Co., Ltd. make)

W-4: Troysol S-366 (made in Troy Chemical)

[0271] The cable address of a basic compound means the following among the above-mentioned table.

N-1: 1 and 5-diazabicyclo [4.3.0]-5-nonene N-2: -- 2, 4, and 5-triphenyl imidazole

N-3:N-hydroxyethyl piperidine N- 4, 2, the 6-diisopropyl aniline N-5:dicyclohexyl

monomethylamine N-6:hexamethylenetetramine N-7:1, and 8-diazabicyclo [5.4.0]-7-undecene

[0272] Furthermore, the cable address of a solvent means the following.

S-1: ethyl lactate S-2:propylene-glycol-monomethyl-ether acetate S-

3:propylene-glycol-monomethyl-ether S-4:2-heptanone S-5: -- ethyl ethoxy propionate

S-6:gamma-butyrolactone S-7: -- butyl acetate [0273] It evaluated as follows about the

transmission of the constituent obtained above, and DOF (defocusing latitude) and LER (the Rhine edge roughness). An evaluation result is shown in Tables 11-12.

[0274] (1) transmissometry -- spin coating of the positive-resist constituent of these was carried out at MgF2 substrate, it carried out \*\*KU during 90 seconds at 100 degrees C using the hot plate, and the resist layer with a thickness of 200nm was created on the MgF2 substrate. The permeability in 157nm was measured using the vacuum-ultraviolet photometer (the Jasco make, VUV200S).

[0275] (2) The antireflection film (ARC25: BURYUWA Saiensu-Sha make) was applied to 600A homogeneity on the silicon substrate by the DOF (defocusing latitude) evaluation spin coater, and stoving was performed for 190 degrees C and 240 seconds. Then, each positive-resist constituent was applied by the spin coater, it heated for 90 seconds and 120 degrees C of resist film with a thickness of 0.3 micrometers were obtained. After performing image formation using a CanonKrF excimer stepper (FPA-3000EX5:NA0.60) and carrying out afterbaking in 110 degrees C and 90 seconds to the obtained resist film, the 0.20-micrometer last shipment pattern was made to form by carrying out present Quercus acutissima in a 0.262-N TMAH water solution. The defocusing latitude (DOF) of 0.20 micrometers was observed in the light exposure reproducing 0.20-micrometer Rhine and a tooth space (= 1/1).

[0276] (3) Evaluation of the LER (Rhine edge roughness) evaluation LER (the Rhine edge roughness) used the length measurement scanning electron microscope (CD-SEM), and measured it about the edge of a 0.20-micrometer Rhine and a tooth space (= 1/1). Within the measurement monitor, the pattern edge was detected in two or more locations, and distribution (3sigma) of the variation in the detection location was made into the index of edge roughness. A value is so desirable that it is small.

[0277]

[Table 11]

表11

実施例	透過率 @157 $\mu$ m[%]	DOF[ $\mu$ m]	LER
27	42	0.7	4.5
28	49	0.7	4.3
29	46	0.7	4.1
30	45	0.8	3.8
31	47	0.7	3.6
32	42	0.7	3.7
33	46	0.8	3.5
34	44	0.6	3.8
35	41	0.7	3.9
36	45	0.8	4.1
37	47	0.7	4.0
38	43	0.9	4.3
39	45	0.8	4.2
40	42	0.8	4.4
41	48	0.7	4.1
42	49	0.7	3.6
43	46	0.7	3.8
44	45	0.8	3.9
45	44	0.7	3.8
46	46	0.8	3.6

[0278]

[Table 12]

表12

実施例	透過率 @157 $\mu$ m[%]	DOF[ $\mu$ m]	LER
47	47	0.8	3.7
48	45	0.7	3.4
49	46	0.7	3.7
50	42	0.8	3.5
51	48	0.7	3.6
52	49	0.7	3.5
53	46	0.7	3.4
54	45	0.8	3.4
55	45	0.8	3.6
56	47	0.7	3.5
57	48	0.7	3.8
58	46	0.8	3.7
59	45	0.7	3.6
60	43	0.8	3.8
61	47	0.8	3.7
62	46	0.7	3.6
63	46	0.9	4.3
64	45	0.7	4.2
65	47	0.8	4.1
66	48	0.7	4.1
67	45	0.8	4.1
68	46	0.7	3.9
69	48	0.7	3.8
比較例4	34	0.4	6.8
比較例5	35	0.5	5.6
比較例6	18	0.6	10.5

[0279] The constituent of this invention has high transmission, and defocusing latitude is large, and the result of Tables 11–12 shows that it is hard to generate the Rhine edge roughness.

[0280] The antireflection film (ARC25, BURYUWA Saiensu-Sha make) was applied to 600A homogeneity on the silicon substrate by the spin coater, and desiccation was performed for 190 degrees C and 240 seconds. Then, after applying each positive-resist constituent by the spin coater, for 120 degrees C and 90 seconds, desiccation was performed and the resist film with a thickness of 0.12 micrometers was obtained. The light exposure of the range of 1 – 100 mJ/cm<sup>2</sup> was irradiated through the mask for adhesion mold exposure to the obtained resist film using laser radiation equipment VUVES-4500 [ 157nm ] (Litho Tech Japan Corp. make). The 0.35-micrometer last shipment pattern was made to form by heating with a hot plate for 110 degrees C and 90 seconds after exposure, and performing a development in a 0.262-N TMAH water solution. In the light exposure reproducing 0.35-micrometer Rhine and a tooth space (1/1), LER (the Rhine edge roughness) and a skirt length configuration were observed as follows.

[0281] (4) Evaluation of the LER (Rhine edge roughness) evaluation LER (the Rhine edge roughness) used the length measurement scanning electron microscope (CD-SEM), and measured it about the edge of a 0.35-micrometer Rhine and a tooth space (1/1). Within the measurement monitor, the pattern edge was detected in two or more locations, and distribution (3sigma) of the variation in the detection location was made into the index of edge roughness. A value is so desirable that it is small.

[0282] (5) Skirt length configuration evaluation dimension size 0.35micrometer Rhine and a tooth-space pattern were observed by SEM (Hitachi Make S-8840), and the following type estimated extent of the skirt length configuration shown in drawing 1 . It is shown that extent of skirt length is so small that a numeric value is small.

A formula  $(B-A) / 2B \times 100$  (%)

[0283] (6) It applied on the silicon wafer which performed hexamethylenedisilazane processing for negative-ized evaluation each positive-resist constituent by the spin coater, stoving was

carried out on the hot plate for 90 seconds at 120 degrees C, and the resist film of 0.1 micrometers of thickness was obtained. The light exposure of the range of 1 mJ/cm<sup>2</sup> - 100 mJ/cm<sup>2</sup> was irradiated to the obtained resist film using laser radiation equipment VUVES-4500 [ 157nm ] (Litho Tech Japan make). It heated with the hot plate for [ 110 degrees-C ] 90 seconds after exposure, and the 0.262-N TMAH water solution performed the development. Thickness was measured after development, and in the high light exposure field of 50 mJ/cm<sup>2</sup> - 100 mJ/cm<sup>2</sup>, what O and a residual membrane are regarded as in what the resist film is dissolving completely was made into x noting that there was concern of negative-izing. The above-mentioned evaluation result is shown in the following table 13.

[0284]

[Table 13]

表 1 3

	LER	裾引き 形状	ネガ化		LER	裾引き 形状	ネガ化
実施例 2 7	5. 0	1 4	○	実施例 5 1	5. 9	1 5	○
実施例 2 8	5. 2	1 3	○	実施例 5 2	5. 0	1 6	○
実施例 2 9	6. 1	1 5	○	実施例 5 3	5. 2	1 4	○
実施例 3 0	5. 9	1 3	○	実施例 5 4	4. 9	1 5	○
実施例 3 1	5. 0	1 4	○	実施例 5 5	5. 1	1 5	○
実施例 3 2	4. 9	1 5	○	実施例 5 6	5. 2	1 6	○
実施例 3 3	5. 1	1 5	○	実施例 5 7	6. 1	1 5	○
実施例 3 4	4. 9	1 6	○	実施例 5 8	5. 9	1 4	○
実施例 3 5	5. 0	1 5	○	実施例 5 9	5. 0	1 3	○
実施例 3 6	5. 2	1 4	○	実施例 6 0	4. 9	1 3	○
実施例 3 7	4. 9	1 3	○	実施例 6 1	5. 1	1 3	○
実施例 3 8	5. 1	1 3	○	実施例 6 2	4. 9	1 5	○
実施例 3 9	4. 9	1 3	○	実施例 6 3	5. 0	1 5	○
実施例 4 0	5. 0	1 5	○	実施例 6 4	5. 2	1 3	○
実施例 4 1	5. 2	1 5	○	実施例 6 5	6. 1	1 4	○
実施例 4 2	6. 1	1 3	○	実施例 6 6	5. 9	1 3	○
実施例 4 3	5. 9	1 4	○	実施例 6 7	5. 0	1 5	○
実施例 4 4	5. 0	1 3	○	実施例 6 8	6. 3	1 5	○
実施例 4 5	4. 9	1 5	○	実施例 6 9	5. 2	1 3	○
実施例 4 6	5. 1	1 5	○	比較例 4	9. 3	3 0	×
実施例 4 7	4. 9	1 3	○	比較例 5	1 0. 8	3. 5	×
実施例 4 8	5. 0	1 4	○	比較例 6	—	—	○
実施例 4 9	5. 2	1 3	○				
実施例 5 0	6. 1	1 3	○				

[0285] The positive-resist constituent of this invention has the small Rhine edge roughness, skirt length is small, and Table 13 shows that the resist film is dissolving completely substantially in evaluation of negative-izing.

[0286]

[Effect of the Invention] By this invention, especially, defocusing latitude is large and it is hard to generate the Rhine edge roughness, sufficient permeability can be shown also in the short wavelength of F2 excimer-laser light (157nm), skirt length of Rhine and a tooth-space pattern is small, and 160nm or less of positive-resist constituents which the resist film dissolves completely substantially and do not have concern of negative-izing can be offered, when negatives are developed with a developer.



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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the skirt length configuration used for evaluation of skirt length of an example.

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[Translation done.]

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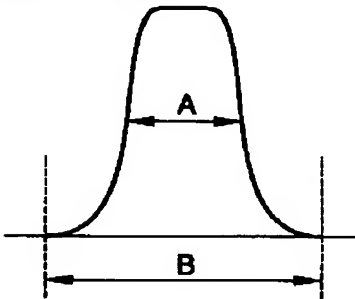
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**DRAWINGS**

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[Drawing 1]



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[Translation done.]